

A MILD, PROTECTIVE AND EFFICIENT PROCEDURE
FOR GRINDING COAL: CRYOCRUSHING

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ABSTRACT

Conventional grinding methods are harsh and produce dramatic changes in coal. When coal, initially at room temperature, is ground in the presence of air, the high localized temperatures produced are known to cause both the production of gases and surface oxidation. These perturbations make meaningful measurements on the product very difficult. A technique that minimizes these effects is the pulverization of coal in liquid nitrogen. Compared with conventional methods, the process is rapid and appears to be less destructive chemically. ESCA measurements support this conclusion. Surface oxidation is significantly reduced by this mild treatment. The method produces more particles below 38 microns than does conventional grinding and these fine particles are less prone to agglomeration.

The crushing of coal presents a considerable challenge to the experimentalist interested in obtaining valid, representative measurements of coal properties. From the moment the coal is broken from the mine face, it begins changing its physical and chemical properties. Not the least of these alterations are the evolution of gases and surface oxidation. By the time the coal reaches the laboratory, it has undergone changes comparable to those it will experience en route to gasification/liquefaction plants. To this extent, the laboratory analyst is dealing with a material similar to that used in these industrial processes. However, further grinding of the coal for laboratory purposes can modify the coal significantly. Radd, Carel and Hamming² have shown that olefinic gases are evolved during the process, presumably as a result of the grinding process itself. This suggests that conventional grinding processes^{3,4} are harsh and produce important changes in coal. The production of heat and the increase of reactive surfaces in an oxidizing environment further modify the coal and make its similarity to the material encountered by the engineers more remote. Thus, every effort must be made to minimize these

¹On sabbatical leave, Philadelphia College of Pharmacy and Science, Philadelphia, Pa.

²F. J. Radd, A. B. Carel and M. C. Hamming, submitted to Fuel.

³G. C. Lowrison, "Crushing and Grinding," Butterworth, p. 33, 1974.

⁴D. I. Hurth, L. S. Sundae and C. W. Schultz, U.S.B.M.R.I. 8069, Twin Cities, Minn., 1975.

effects. A technique discovered independently in this laboratory and recently reported elsewhere^{5,6} appears to achieve this.

EXPERIMENTAL WORK

Air-dried coal (approximately 0.65 cm stock) is placed in a Dewar flask containing liquid nitrogen. All but a few milliliters of the liquid nitrogen are decanted and the deep-frozen coal is transferred rapidly to a hammermill.⁷ The issuing product, considerably below room temperature, is collected in a plastic bag and is surrounded by nitrogen vapors rising from the coal. This is in contrast to grinding using a mini-ball mill (Wiggle-bug Model LP60) where the issuing coal is hot to the touch. The ground samples are quickly transferred to a sieve⁸ for sizing and sealing for later experimentation.

RESULTS AND DISCUSSION

While grinding of polymeric materials at reduced temperatures has been noted in the English literature,³ this laboratory is unaware of any such study on coal. Recent abstracts in Japanese⁵ and Russian⁶ publications suggest many parallels to this work. These papers have been received and are being translated.

That precooling the coal to liquid nitrogen temperature produced dramatic effects on the ground product is evident from Table I. Samples (100 g) of Illinois No. 6 coal were ground under a variety of conditions: namely, in air at ambient temperature, with dry ice, and in liquid nitrogen. The ground coal was rapidly sieved into fractions between 500 and 90 microns, between 90 and 38 microns, and a fraction below 28 microns. The latter fraction was further analyzed with a Coulter Counter^{9,10} and the results were presented in Table I. Whereas regular grinding, i.e., at initial ambient temperature in air, resulted in a particle size distribution that averages near the 90 micron size, those grindings at reduced temperatures produced average particles closer to the 38 micron size. Nearly a third of the coal that was freeze-ground in liquid nitrogen passed the 38-micron sieve compared with 7.7 percent for the regularly ground coal. These percentages are remarkably reproducible. Furthermore, the Coulter Counter study of the particle distributions showed the most probable particle size in this fraction to be 28 microns for the regular grind and 18 microns for

⁵E. Nakanichi and K. Toyotate Funsai (Micromeritics) 18, 94 (1973) via Chem. Abstr. 81, 171948.

⁶T. Khrenkova, V. Lebedev, N. Goldenko and G. Glovina, Khim. Tverd. Topl. 1975, 11; via Chem. Abstr. 83, 13132.

⁷Micropulverizer 67J1431, Slick Company, Summit, N.J.

⁸Type 03.501 #720 Manufactured by Alfred Fritch for the Geos Corporation.

⁹T. Allen, "Particle Size Measurement," 2nd ed., John Wiley & Sons, N.Y., 1975.

¹⁰We are indebted to F. Radd, Continental Oil Company, Ponca City, OK for these analyses.

TABLE I
Particle Size Distributions Reported in Grams and as % Recovery

Sample	Size in Microns							Most Probable size -38 Fraction (Coulter Counter)
	+500 g	+500 %	-500 g	+90 %	-90 g	+38 %	-38 g	
Air (ambient)	---	---	21.5	34.7	35.7	57.6	4.8	28 microns
N ₂ (k) (air-dried coal)	0.2	0.3	19.4	25.5	32.3	42.4	24.2	18 microns
N ₂ (k) (wet coal)	---	---	18.9	26.6	27.0	38.0	25.2	not measured
N ₂ (k) (double ground)	---	---	6.3	13.9	22.0	48.3	17.2	not measured
CO ₂ (s)	0.1	0.2	19.9	37.0	23.5	43.5	10.5	not measured

*After one week, agglomeration reduced this fraction by 40%.

**After one week, agglomeration reduced this fraction by 10%.

the liquid-nitrogen-ground coal. The fraction ground at dry ice temperature was not subjected to Coulter Counter analysis but might be expected to be intermediate since the sieve classification is intermediate.⁴

It should be noted that care must be exercised both in the grinding process and in handling of the ground product. Considerable loss of ultra-fine coal dust was evident during the grinding. For health reasons as well as for scientific study, it would be advantageous to recover these colloidal particles, which could be a most valuable fraction; possibly a shrouded mill could be used. The surface properties of the -38 micron fractions were considerably different than those of other fractions. A second sieving for a longer period (thirty minutes versus the original ten minutes) showed that forty percent of the regularly ground coal failed to pass the 38 micron screen, whereas all but ten percent of the liquid-nitrogen-ground coal did so. Of course, one recovers more of the -38 micron fraction with further increases in sieving time, but this is likely due to the abrasive nature of the sieving process itself. Thus, it appears that the coal ground with liquid nitrogen is not only more friable, but is less prone to agglomeration.

Even under the mild grinding conditions produced by liquid nitrogen, some interaction with oxygen will occur. Coal has trapped in its inner pores^{2,10} significant quantities of gases, about eighteen percent of which is oxygen. These gases are not removed by pumping under vacuum, but probably are released during the grinding operation. Some of these gases can be displaced by treating the coal with methanol, shown by Fugassi¹¹ to swell the coal structure. Experiments performed in this laboratory show that methanol releases three to ten cc of gas, predominantly air, at STP per ten grams of Illinois coal. The enormously increased surface produced when a 0.65-cm coal fragment (surface area ~2.5 cm²) is reduced to 25 micron cubes on edge (surface area 600 cm²) can scavenge a significant fraction of the oxygen liberated by the grinding process.

Such a dramatic increase in surface area caused by efficient grinding might be expected to result in major differences in the ESR spectrum of the ground product. However, no differences in the spectra of coal ground in liquid nitrogen and of coal ground in air were observed in any of the sieved fractions. Aging of coal ground in air did produce an increase in ESR absorption; presumably this was due to oxygen uptake. A study of this phenomenon is planned in the near future.

The most informative and startling experiment that distinguished the products of the two grinding methods involved sedimentation rates in a polar solvent mixture (1:1 toluene-methanol). Samples (0.5 g) of -38 micron fractions from the regular grind and the liquid-nitrogen grind were suspended in fifty cc of the solvent mixture. Although the liquid-nitrogen-ground sample had a smaller particle size, it settled out about 100 times as fast as the regularly ground coal. Because this striking difference

¹⁰J. A. Solomon and R. J. Enright, Proceedings 8th Biennial Conference of the International Briquetting Association, pp. 61-71, Denver, CO., 1963.

¹¹J. P. Fugassi and M. Mitchell, Jr., "Coal Science," Adv. Chem. Ser. 55, 400 (1966).

persists for several weeks, it reflects permanent changes in these samples. Our interpretation is that the regularly ground coal experienced extensive oxidation during the grinding and developed a more polar surface which interacts more strongly with the methanolic solvent so that the settling rate is reduced. Regardless of whether this explanation is correct, the experiment indicates a drastic difference in the surface-solvent interaction for these differently ground coal samples. The toluene-methanol extracts of these samples are being analyzed by HPLC for further comparison. An alternative explanation that is not supported by ESCA analyses (vide infra) is that the product ground in liquid nitrogen is less homogeneous, and results in more of the dense ash in the -38 micron fraction. However, since this fraction was nearly a third of the sample and greatly exceeds the ash content of Illinois No. 6 coal, it could provide only a partial explanation for the rapid settling rate of the liquid-nitrogen-ground coal.

The -38 micron fractions of air-ground and liquid-nitrogen-ground coal were submitted for ESCA analysis using a Hewlett-Packard Model 5950A photoelectron spectrometer equipped with an aluminum anode. The samples were heavily coated on double sticky tape and were evacuated overnight to $\sim 1 \times 10^{-9}$ torr prior to analysis. Charging effects were minimized by flooding the sample with electrons and biasing it slightly negative. The data are presented in Figures 1 and 2 where the 50K (counts per inch) survey scans show an oxygen carbon ratio of 0.48 for the air-ground coal and a 0.25 ratio for the liquid-nitrogen-ground coal (using standard sensitivity factors).¹² Because of the low pressures involved and sample handling procedures, the oxygen analysis is believed to represent chemically bound oxygen and not adsorbed oxygen.¹³ Further, the 5K insert scans show that there is not a significant concentration of silicon, aluminum, or sulfur in the liquid-nitrogen-ground coal. If an enrichment in these elements occurred, it was in the air-ground fraction. Finally, it should be observed that nitrogen incorporation onto the coal surface during grinding was negligible. The 5K insert scans suggest 1.2 ± 0.1 atom-percent of nitrogen in both samples. This is consistent with the macroscopic elemental analysis. These spectra, coupled with the observation that the ESCA analysis for oxygen in the liquid-nitrogen-ground sample ($\sim 20\%$) compares favorably with that by neutron activation ($19.55 \pm 0.16\%$)^{14,15} suggests that the liquid-nitrogen-ground coal surface more accurately represents the bulk or macroscopic structure of the coal.

ACKNOWLEDGMENTS

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¹²C. D. Wagner, Anal. Chem., 44, 1050 (1972).

¹³D.C. Frost, W. Leeder, and R. Tapping, Fuel 53, 206 (1974).

¹⁴We are grateful to Professor Volborth, Department of Chemistry, North Dakota State University, Fargo, N.D. 58102, for these analyses.

¹⁵G. Miller and A. Volborth, "Use of 14-Mev Neutron Generator in Analysis of Coal and Coal Derivatives," Small Accelerator Conference, Denton, Texas, Oct. 25-27, 1976.

ESCA SPECTRA OF ILLINOIS NO. 6 COAL
(-38 MICRON FRACTION, AIR-GRIND)

SENSITIVITY FACTOR: 50K
(5K FOR INSETS)

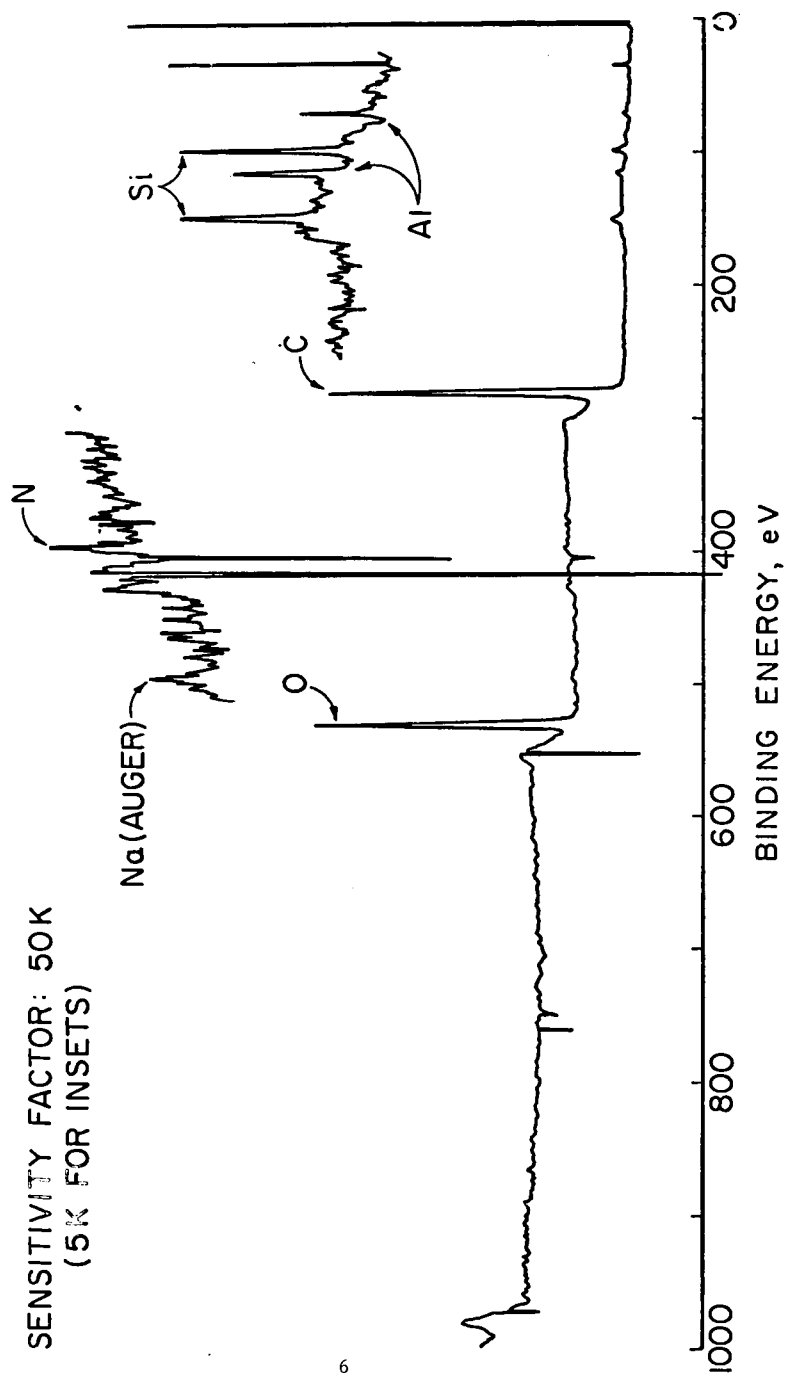


Figure 1

ESCA SPECTRA OF ILLINOIS NO. 6 COAL
(-38 MICRON FRACTION, LIQUID N₂ GRIND)

SENSITIVITY FACTOR: 50 K
(5 K FOR INSETS)

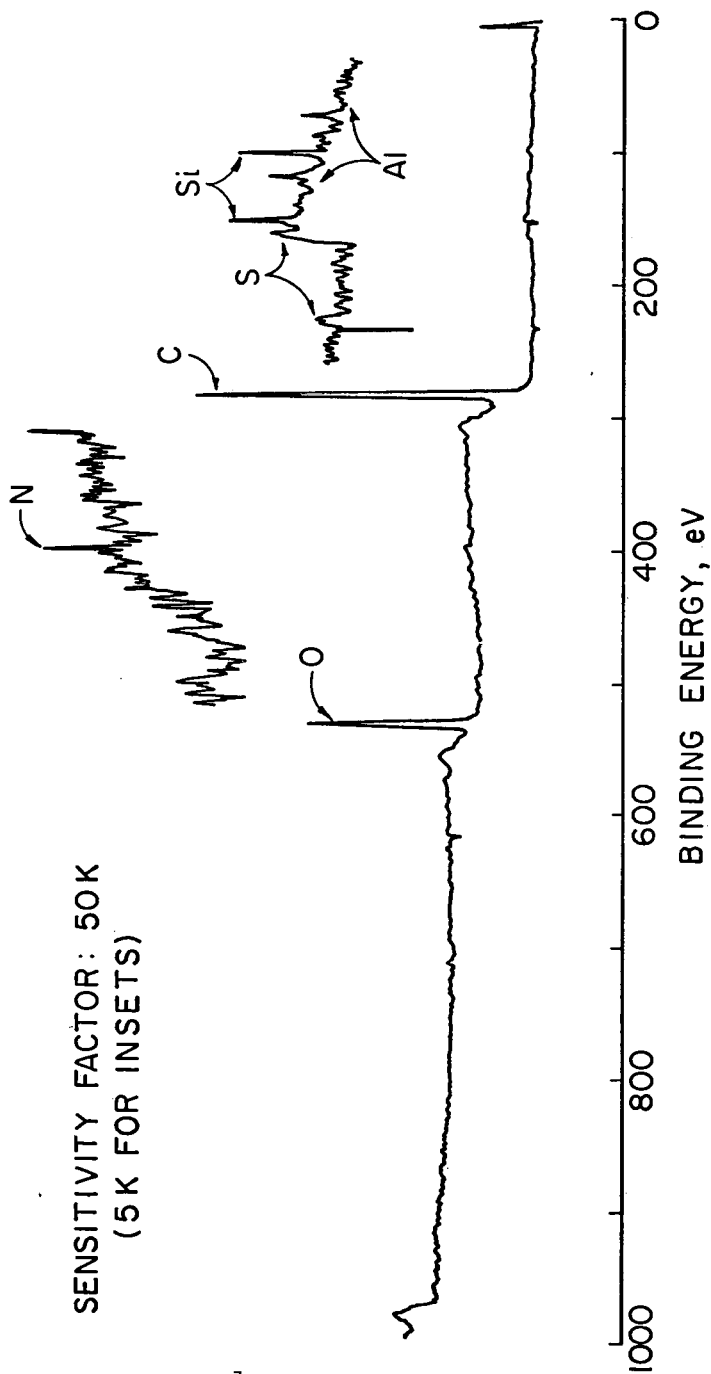


Figure 2

DETERMINATION OF TETRALIN AND NAPHTHALENE IN A COAL-DERIVED SOLVENT

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Introduction

There are a variety of methods currently in use for the separation and characterization of components in coal liquids. Most involve fractionation into various classes of compounds which are subjected to further analysis. Sternberg *et al.* (1,2) divided coal conversion products into asphaltenes and oils. These main constituents were further subdivided by column chromatography and precipitation. Slightly modified separation and characterization methods developed by the Bureau of Mines - API Research Project 60 for characterizing heavy ends of petroleum were used successfully in analyzing coal liquid distillates within the boiling range 200° to 540°C (3). Farcasiu (4) developed an alternative scheme based on separation of fractions of different chemical functionality using sequential elution of the fractions from silica gel. Process solvents and liquefaction products were separated into saturates, aromatics, and various polar materials with neutral alumina by Schiller (5) and then subjected to GC/MS analyses. After preparative separation using gel permeation chromatography various coal liquid fractions were studied by quantitative ¹H and ¹³C Fourier transform nuclear magnetic resonance techniques by Dorn *et al.* (6,7). Raw anthracene oil was separated using cation, anion, and complexation chromatography by Scheppelle *et al.* (8,9). They studied some of the fractions with low- and high-resolution field ionization mass spectrometry. Prather *et al.* (10) used high-performance liquid chromatography (HPLC) to characterize creosote oil during hydrogenation/hydrodesulfurization of the oil.

Tetralin is important in the study of the hydrogen donor capacity of recycle solvents (11, 12-14). A measure of tetralin in recycle solvents can be obtained by gas-liquid chromatography using a Dexil 300 liquid phase to obtain simulated boiling-point distributions (11). This type of approach is useful but can result in complex chromatograms and is subject to interferences (15).

In this study an analytical method was developed to determine specifically tetralin and naphthalene in a Wyodak coal-derived solvent from the Southern Services Inc. SRC plant located at Wilsonville, Alabama. Several other hydro-aromatic and polycyclic aromatic hydrocarbons were also separated from the solvent and identified. Aluminum oxide open-column chromatography, μ -Bondapak

C₁₈ high-performance liquid chromatography and fluorescence spectroscopy were combined to give qualitative and quantitative information on tetralin and naphthalene in the coal-derived solvent which was hydrogenated under different conditions.

Experimental

Apparatus. The high-performance liquid chromatograph used was a Waters model ALC/GPC 244 equipped with a model 6000-A pump, a U6K injector, and a free standing ultraviolet detector set at 254 nm. A stainless steel tube 11 cm x 0.23 mm I.D. attached to the exit port of the detector cell was used in sample collection. A μ -bondapak C₁₈ column with methanol:water (65:35) at a flow rate of 1 ml/min was employed, and a 10 mv recorder completed the system.

The columns used in open column chromatography were 50 cm x 11 mm I.D. Pyrex (Corning #2145) and were dry packed to a height of 35 cm with aluminum oxide activity II-III according to Brockmann (aluminum oxide from I.C.N. Life Sciences, Cleveland, Ohio and Brinkmann, Westbury, N.Y. were used interchangeably). Columns packed with silica gel (Brinkmann) were prepared in the same manner. Brinkmann ALOX N/UV 254 thin-layer chromatoplates were used in the thin-layer chromatography (TLC) work with n-hexane as the mobile phase.

Reagents. Pure grade (99% min) n-hexane was obtained from Phillips Chemical. Glass distilled methanol from Burdick and Jackson, and glass distilled water were filtered prior to mixing.

Naphthalene (99+%) and Tetralin (99%) were obtained from Aldrich and used as received. All other chemicals were obtained from commercially available sources and were purified when necessary.

Recycle Solvents. Recycle solvent from the liquefaction of Wyodak Coal at Wilsonville, Alabama (designated F-1) was hydrogenated at 2000 psi initial hydrogen pressure at 700°F for 1 hr over a Co-Mo on Al₂O₃ catalyst (Nalcoma 471). The product was designated F-2. Hydrogenation of the original solvent at 3000 psi initial hydrogen pressure at 800°F for 1 hr over the same catalyst resulted in a product designated F-3. The nominal boiling range of the three solvents was from 177-427°C (350-800°F).

Procedures.

Preparation of samples with no hexane insolubles (F-3). 20 g of sample was brought to volume with n-hexane in a 100 ml volumetric flask. Aliquots of 25 ml were added to each of three 50 ml volumetric flasks. Standard additions of 50 mg and 100 mg each of tetralin and naphthalene were added volumetrically to two of the flasks, respectively. All three flasks were diluted to volume with n-hexane. Aliquots of 1 ml of each of the solutions were pipetted onto the top of each of three aluminum oxide columns. Elution was performed with n-hexane. Work with standards showed that the tetralin was eluted totally in the first 15 ml (Fraction 1) and the naphthalene in 15-55 ml (Fraction 2). Fraction 1 was collected in a 25 ml volumetric flask and Fraction 2 in a 50 ml volumetric flask, each flask diluted to the appropriate

volume with n-hexane.

Preparation of samples with hexane insolubles (F-1 and F-2). Hexane insolubles coat the volumetric glassware when the sample solution is less than about 25% w/v in n-hexane. The volume displacement was found to be approximately 0.5 ml for a 20 g sample. To minimize this source of error, a solution of 20 g sample in approximately 120 ml n-hexane was made and swirled in a sealed flask. After at least two hours, most of the solid material coated the flask, and the remaining solution was rinsed into a 250 ml volumetric flask, then made up to volume. Three aliquots of 25 ml each were prepared as before, but the standard addition quantities were 20 mg and 50 mg for both tetralin and naphthalene. Aliquots of 2 ml were pipetted onto the aluminum oxide columns and Fraction 1 and Fraction 2 collected.

Determination of tetralin and naphthalene. Determination of tetralin in F-1, F-2 and F-3 was accomplished by an injection of 10 μ l of each of the unknown and two standard addition solutions onto the μ -bondapak C₁₈ column with the detector at 0.01 absorbance units. The heights of the tetralin peaks were all measured and were "normalized" to the peak height of the only other predominant chromatographic peak in Fraction 1 which was identified as indan. This internal reference peak represented a constant amount of indan present in the unknown and two standard addition solutions for a given sample. Normalization of all the tetralin peak heights to a constant indan peak height compensated for the non-reproducible injections inherent in the HPLC system. A standard addition curve was prepared by plotting peak height vs mg tetralin added. The line intersecting the peak height axis was extrapolated to zero peak height to obtain the tetralin concentration in the prepared solution. From this value the percentage tetralin was calculated (Figure 1).

Injectons of 10 μ l at 0.1 absorbance units were used for the determination of naphthalene. Peak heights were normalized to the predominant peak at 18.4 ml elution volume, which was believed to be composed mainly of biphenyl and 2-methylnaphthalene. The percentage naphthalene was calculated in the same manner as tetralin.

Peak identification. An appropriate amount of sample or standard solution was injected onto the μ -bondapak C₁₈ column, and peaks collected directly into a 1x1 cm quartz cuvette. Final volume was made up to 3-4 ml, and fluorescence excitation and emission spectra taken. Spectra were then compared with standard spectra taken from standards run through the aluminum oxide-HPLC system.

Results and Discussion

Initial Experiments. Initial exploratory work was performed with one or two μ -bondapak C₁₈ columns used singly or connected in series with methanol:water (70:30) as a mobile phase at 1 ml/min. Fluorescence spectra were employed for chromatographic peak identification, as very dilute samples can be analyzed without any preconcentration steps. Samples thought to contain tetralin were separated on the μ -bondapak C₁₈ columns and were collected from 20 μ l injections of the first 50 ml of n-hexane eluted from both silica gel and aluminum oxide columns charged with approximately 100 mg of F-1. Fluorescence spectra showed two components present in the chromatographic sample

collected at the elution volume for tetralin. Tetralin was one component with an emission maximum at 286 nm, and an unknown, with emission maxima at 324 and 339 nm. An excitation spectrum of the interferent was taken by setting the emission monochromator at 360 nm. Comparing the unknown's excitation maxima with the maxima of several published ultraviolet absorption spectra (16) led to the assumption that the unknown was an alkyl-substituted naphthalene. It was later identified as acenaphthene by fluorescence spectroscopy. In order to remove this interferent, two separate fractions had to be collected, one containing tetralin and the other acenaphthene. Both silica gel and aluminum oxide columns, prepared as before, were investigated. It was assumed that in both systems tetralin would elute first and naphthalene would elute slightly before acenaphthene. The desired separation would, therefore, provide a fraction containing all the tetralin (Fraction 1), and a second fraction containing naphthalene and acenaphthene (Fraction 2).

Approximately 10 mg each of tetralin and naphthalene were placed on top of individual columns packed with each adsorbant. Samples were collected every 5 ml, diluted to an appropriate volume, and absorbance data obtained. Results were plotted as percentage of the total absorbance of all samples at 273 nm for each sample vs ml eluted (Figures 2 and 3). 98.5% of the tetralin eluted from the aluminum oxide column before the naphthalene started to elute, while only 44.2% eluted from silica gel before naphthalene started to elute. Thus, aluminum oxide provided a relatively clean separation of tetralin and naphthalene, whereas silica gel did not. To check if tetralin was separated from acenaphthene with the aluminum oxide system, samples corresponding to the chromatographic peaks at the elution volume of tetralin from a μ -bondapak C₁₈ column were collected for both Fractions 1 and 2 from F-1. Fluorescence excitation and emission spectra were obtained for each sample. The fluorescence spectra indicated the chromatographic peak from Fraction 1 was tetralin, and the chromatographic peak from Fraction 2 gave a fluorescence excitation and emission spectra identical to acenaphthene (Figures 4-7). These results indicated that tetralin was separated from acenaphthene.

Sample size studies were performed with aluminum oxide columns with F-1. Sample sizes of 1000, 500, and 200 mg overloaded the column to the extent that naphthalene was present in Fraction 1. Acenaphthene was also present in Fraction 1 with sample sizes of 1000 and 500 mg, but not 200 mg. Sample sizes of 100 and 50 mg resulted in a clean separation of tetralin and naphthalene with no interference from acenaphthene.

Precision and Accuracy of the Method. The precision of the method for five replicate determinations of tetralin and naphthalene on F-3 was quite good, yielding results at the 95% confidence level of $6.11 \pm 0.030\%$ for tetralin and $6.36 \pm 0.043\%$ for naphthalene (Table I).

Results of analysis of F-1, F-2, and F-3 at two different sample size levels illustrate the absence of any significant constant error (Table II). The average results for naphthalene in F-1 and F-2 were identical for two different sample sizes, and the other tetralin and naphthalene results showed no significant deviation. Spiking experiments for each sample at two levels of tetralin and naphthalene indicated good percentage recovery (Tables III and IV). The pretreatment for removal of hexane-insolubles from F-1 and F-2

described in Experimental did not appear to cause any significant loss of tetralin and naphthalene.

Identification of Tetralin, Indan and Naphthalene. Chromatographic peaks corresponding to tetralin, indan, and naphthalene each from F-1, F-2 and F-3 were all collected from the μ -bondapak C_{18} column after separation on aluminum oxide columns. The fluorescence excitation and emission spectra were obtained and were compared with excitation and emission spectra of standards treated chromatographically in an identical manner (Figures 8-11). Comparison of the sample excitation and emission spectra with the corresponding standard excitation and emission spectra shows very good comparison for the respective compounds. The fluorescence excitation and emission spectra of tetralin (Figure 4) and indan (Figure 8) are identical. However, because of the chromatographic systems used these compounds are separated completely. These results show how fluorescence spectroscopy can be used in combination with chromatographic techniques in the analysis of complex samples like coal-derived solvents.

Internal Reference Standard. A basic assumption in using an internal reference peak from the sample chromatogram for the standard addition method is the reference peak represents the same amount of internal reference compound in all solutions used in a determination and thus the same chromatographic peak heights. At one point a new batch of aluminum oxide was used and erratic reference peak heights in the naphthalene fraction were noticed. The collection of Fraction 2 was made from 15-50 ml, and a change to 15-55 ml rectified the problem indicating that all the internal reference compound was not obtained in the first collection. As a precaution against nonuniformity within a given standard addition series, the amount of aluminum oxide placed in the glass column was weighed, and was kept uniform for a given batch of adsorbant. Chromatograms of both Fractions 1 and 2 from F-1 show the positions of the internal reference peaks, tetralin peak and naphthalene peak (Figures 12 and 13). The peak corresponding to indan was the internal reference for Fraction 1, and the peak for biphenyl and 2-methylnaphthalene was the internal reference for Fraction 2.

Limits of detection were calculated at maximum detector absorbance settings of 0.01 for tetralin and 0.1 for naphthalene. Since baseline noise at these settings is minimal, the smallest practical measurable peak height was chosen arbitrarily to be 2 mm. Typically observed standard addition curve slopes of 10 mm/mg for tetralin and 17 mm/mg for naphthalene were used. For a 100 mg sample, this would correspond to limits of detection for the method as described of 0.2 mg tetralin, or 0.2% tetralin, and 0.1 mg naphthalene, or 0.1% naphthalene. These limits could be lowered by increasing the detector sensitivity or concentrating the hexane fractions. All anticipated samples fall well above these limits.

R_f Values and Retention Volumes of Several Hydroaromatic and Polycyclic Aromatic Hydrocarbons. R_f values from thin-layer chromatography and retention volumes from HPLC for the compounds studied are given in Table V. Aluminum oxide separations with the appropriate mobile phase occur mainly by aromatic ring number (17). Compounds with the greater number of aromatic rings are retained more strongly. The separation mechanism on a μ -bondapak C_{18} column is not as clear (18). It has been shown that the retention volumes of aromatic hydrocarbons generally increase with increasing carbon number on columns of Zipax Permaphase

ODS in water-methanol mixed solvents (19). The retention volumes of substituted alkyl derivatives of aromatic compounds indicated that these compounds separated with increasing aliphatic carbon number. However, without prior information as to the parent compound type, approximate capacity factors are difficult to estimate (19).

The R_f values and retention volumes obtained in this work (Table V) suggest the possibility of developing an overall characterization scheme for aromatic and hydroaromatic hydrocarbons in coal liquid samples. This is presently under investigation. Also the data in Table V indicate the importance of initial separation with aluminum oxide. For example, with the compounds in Table V, four main fractions could be initially separated with aluminum oxide. These fractions would contain compounds 1-6, 7-19, 20-22, 23-25 respectively. Further separation of each fraction with μ -bondapak C_{18} would give almost complete separation of each compound in a given fraction. Phenanthrene and fluorene would have nearly the same retention volumes and 2-methylnaphthalene and biphenyl would have nearly the same retention volumes. However, with refinements in the chromatographic systems, it should be possible to achieve complete separation of these compounds.

The results in Table V show that it was necessary to obtain two fractions from the coal-derived solvents to determine tetralin and naphthalene. Acenaphthene and tetralin have identical retention volumes on μ -bondapak C_{18} , thus necessitating the initial separation step with aluminum oxide.

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Table I

Precision of the Method with F-3

<u>Sample weight, mg</u>	<u>Tetralin, %w/w</u>	<u>Naphthalene, %w/w</u>
97.92	6.08	6.36
97.92	6.13	6.40
97.92	6.10	6.38
96.67	6.10	6.31
96.67	6.14	6.34
	$\bar{x} = 6.11$	$\bar{x} = 6.36$
	$s = 0.024$	$s = 0.035$

95% confidence level

tetralin: $6.11 \pm 0.030\%$

naphthalene: $6.36 \pm 0.043\%$

Table II

Variation of Sample Size

Sample	Weight, mg	Tetralin, %w/w	Average	Naphthalene, %w/w	Average
F-3	96.67	6.10		6.31	
	96.67	6.14	6.12	6.34	6.32
	48.93	6.13		6.40	
	48.93	6.15	6.14	6.36	6.38
F-2	81.20	2.71		7.09	
	81.20	2.73	2.72	7.03	7.06
	43.61	2.77		7.08	
	43.61	2.73	2.75	7.04	7.06
F-1	85.29	2.24		7.27	
	85.29	2.32	2.28	7.33	7.30
	44.24	2.24		7.28	
	44.24	2.28	2.26	7.32	7.30

Table III

Percentage Tetralin Recovery in Spiked Samples

Sample	Weight, mg	Tetralin ^a Present, mg	Tetralin Added, mg	Tetralin ^b Found, mg	Recovery, %
F-3	95.79	5.86	0.96	0.96	100
	95.79	5.86	0.96	1.01	105
	96.67	5.92	2.41	2.33	97
	96.67	5.92	2.41	2.46	102
					<hr/> $\bar{x} = 101$
F-2	86.32	2.36	0.77	0.77	100
	86.32	2.36	0.77	0.74	96
	84.60	2.32	1.93	1.98	102
	84.60	2.32	1.93	1.91	99
					<hr/> $\bar{x} = 99$
F-1	84.98	1.93	0.78	0.72	92
	84.98	1.93	0.78	0.73	94
	81.02	1.84	1.95	1.92	98
	81.02	1.84	1.95	1.89	97
					<hr/> $\bar{x} = 95$

^aResults obtained from the standard addition method.

^bResults corrected for original tetralin content present in the sample.

Table IV

Percentage Naphthalene Recovery in Spiked Samples

Sample	Weight, mg	Naphthalene ^a Present, mg	Naphthalene Added, mg	Naphthalene ^b Found, mg	Recovery, %
F-3	95.79	6.09	0.87	0.85	98
	95.79	6.09	0.87	0.83	95
	96.67	6.15	2.18	1.98	91
	96.67	6.15	2.18	2.02	93
				average	94
F-2	86.32	6.09	0.70	0.65	93
	86.32	6.09	0.70	0.71	101
	84.60	5.97	1.75	1.81	103
	84.60	5.97	1.75	1.80	103
				average	100
F-1	84.98	6.20	0.69	0.68	99
	84.98	6.20	0.69	0.66	96
	81.02	5.91	1.73	1.66	96
	81.02	5.91	1.73	1.69	98
				average	97

^aResults obtained from standard addition method.

^bResults corrected for original naphthalene content present in the sample.

Table V

R_f Values and Retention Volumes^a of Hydroaromatic
and Polycyclic Aromatic Hydrocarbons

Compound	R_f Value	Retention Volume, ml
1) benzene	--	6.3
2) 1,2,4-trimethylbenzene	--	19.5
3) 1-phenyldodecane	--	No indication of elution
4) tetralin	0.74	21.5
5) indan	--	14.8
6) 5-methyltetralin	--	33.0
7) indene	0.55	10.5
8) naphthalene	0.50	11.7
9) acenaphthene	0.44	21.5
10) 1,5-dimethylnaphthalene	0.43	26.8
11) 1-methylnaphthalene	0.43	17.6
12) biphenyl	0.43	18.3
13) 2-methylnaphthalene	0.42	18.4
14) 2,3-dimethylnaphthalene	0.40	27.3
15) 1-phenyl-3,4-dihydronaphthalene	0.38	55.2
16) 9,10-dihydroanthracene	0.34	26.1
17) acenaphthylene	0.32	14.6
18) 9,10-dihydrophenanthrene	0.27	30.3
19) [2.2] paracyclophane	0.24	32.8
20) fluorene	0.20	25.2
21) anthracene	0.14	28.0
22) phenanthrene	0.13	25.0
23) pyrene	0.069	39.6
24) fluoranthene	0.056	36.9
25) chrysene	0.054	62.1

^aOne μ -bondapak C₁₈ column with methanol:water (65:35) at 1 ml/min.

FIGURES

- Figure 1 Standard addition curve for determination of tetralin.
- Figure 2 Elution of tetralin and naphthalene from silica gel.
- Figure 3 Elution of tetralin and naphthalene from aluminum oxide.
- Figure 4 Fluorescence excitation and emission spectra of standard tetralin.
- Figure 5 Fluorescence excitation and emission spectra of tetralin peak collected from Fraction 1 of F-1.
- Figure 6 Fluorescence excitation and emission spectra standard acenaphthene.
- Figure 7 Fluorescence excitation and emission spectra of acenaphthene peak collected from Fraction 2 of F-1.
- Figure 8 Fluorescence excitation and emission spectra of standard indan.
- Figure 9 Fluorescence excitation and emission spectra of indan peak collected from Fraction 1 of F-1.
- Figure 10 Fluorescence excitation and emission spectra of standard naphthalene.
- Figure 11 Fluorescence excitation and emission spectra of naphthalene peak collected from Fraction 2 of F-1.
- Figure 12 HPLC chromatograms of Fraction 1 from F-1 and F-3.
- Figure 13 HPLC chromatogram of Fraction 2 from F-1.

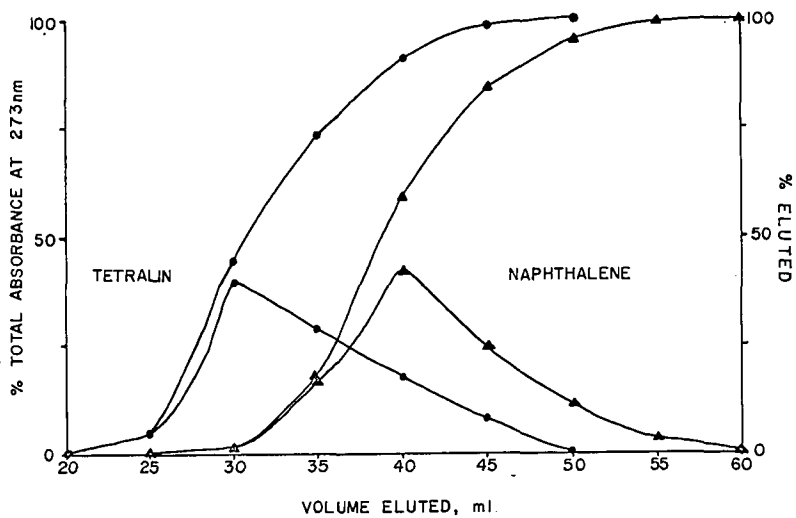


Figure 2

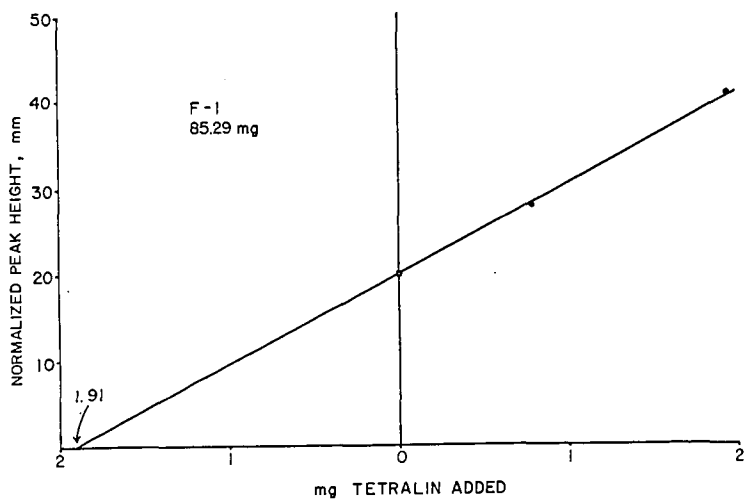
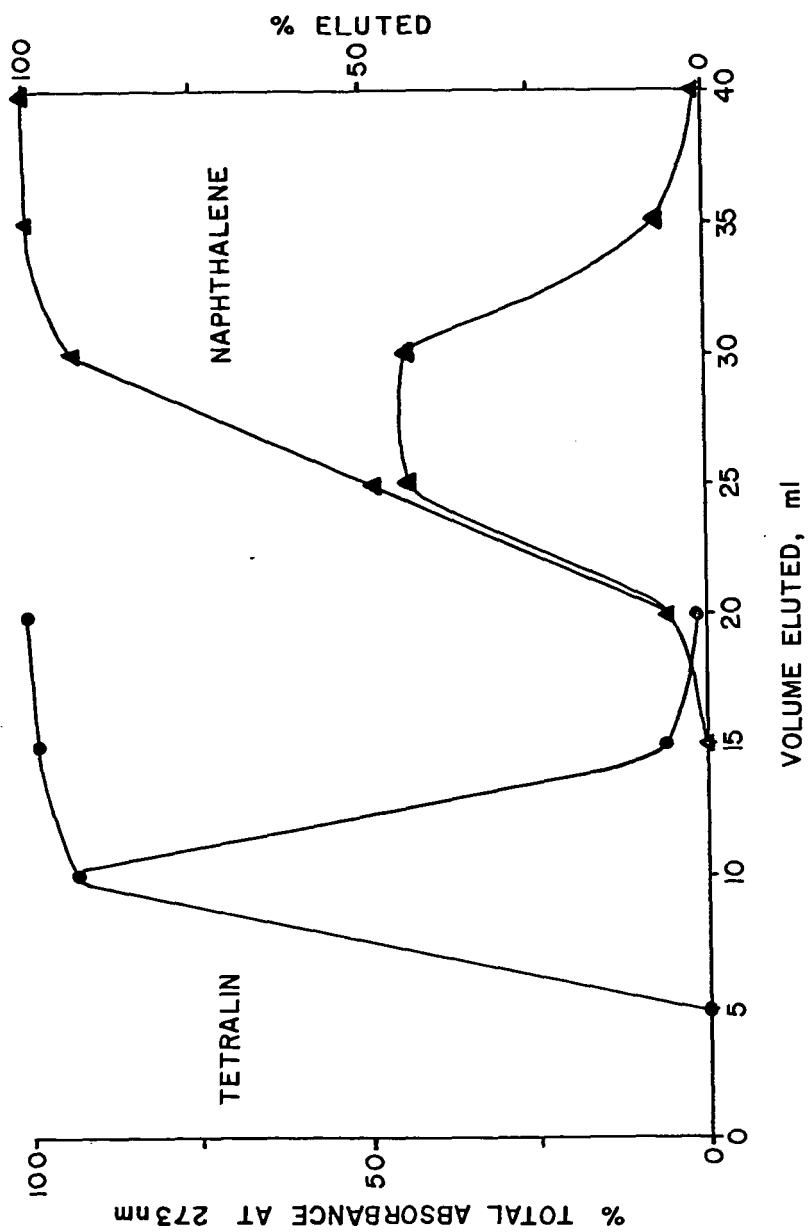
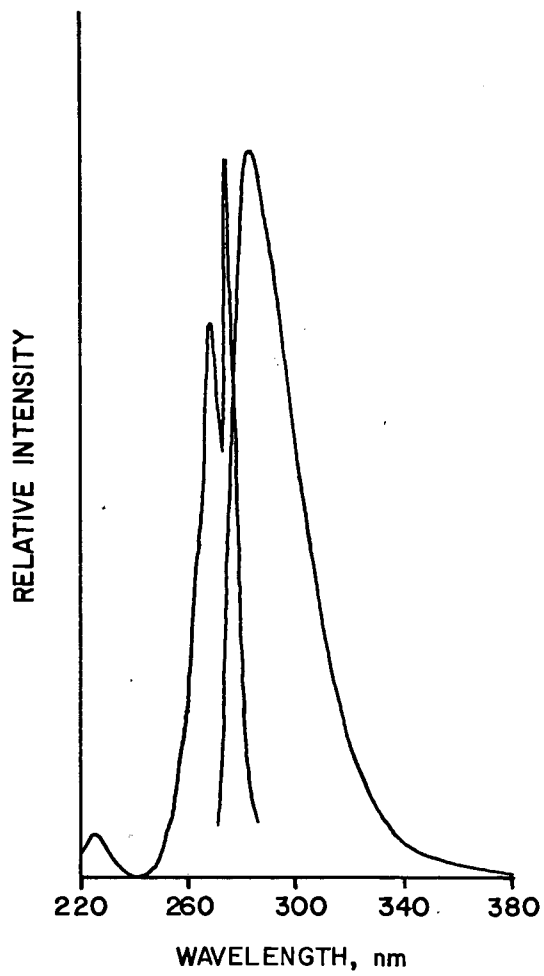
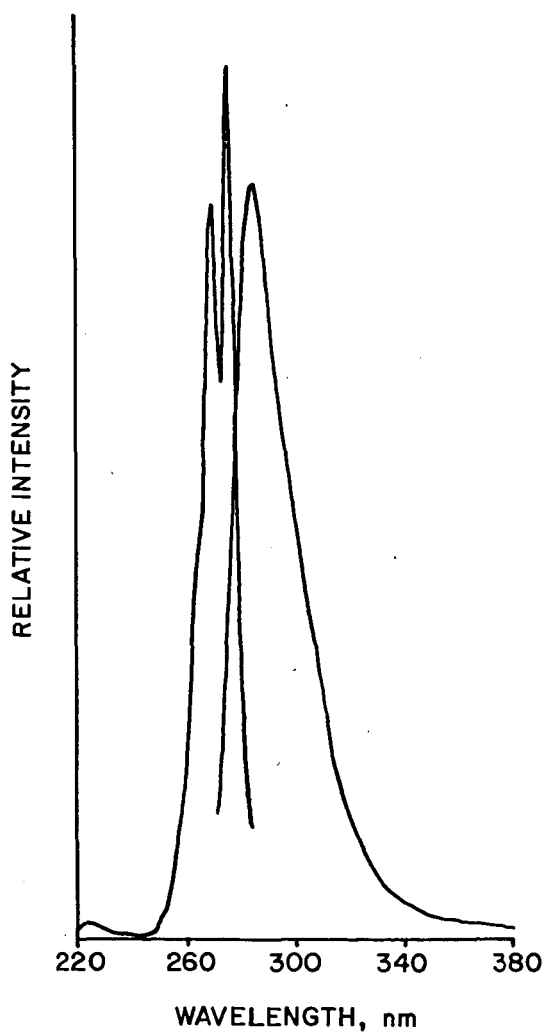
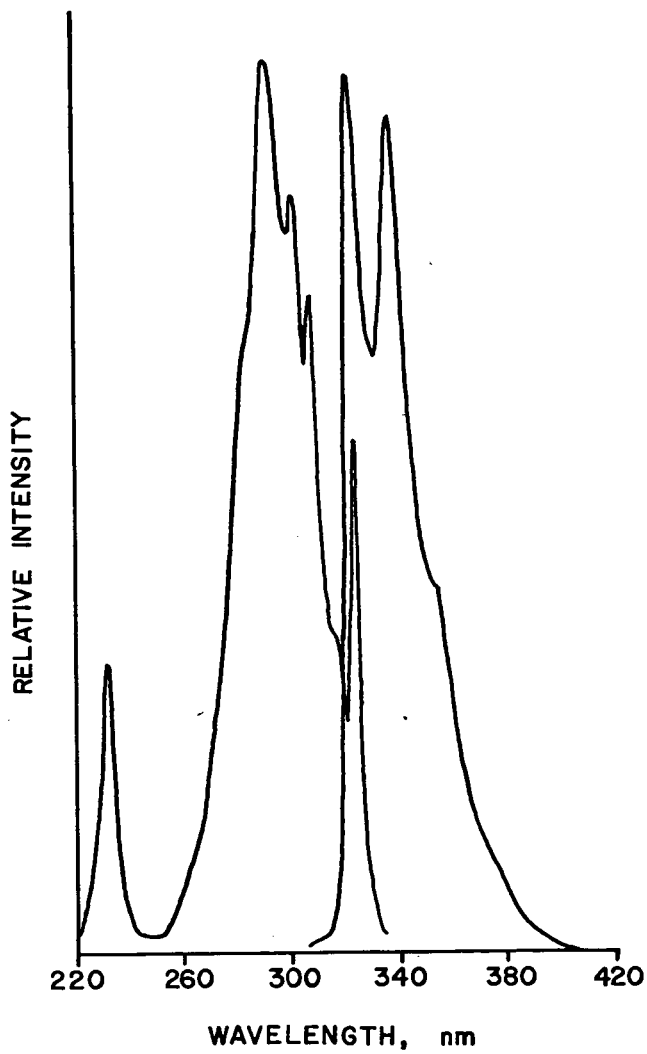


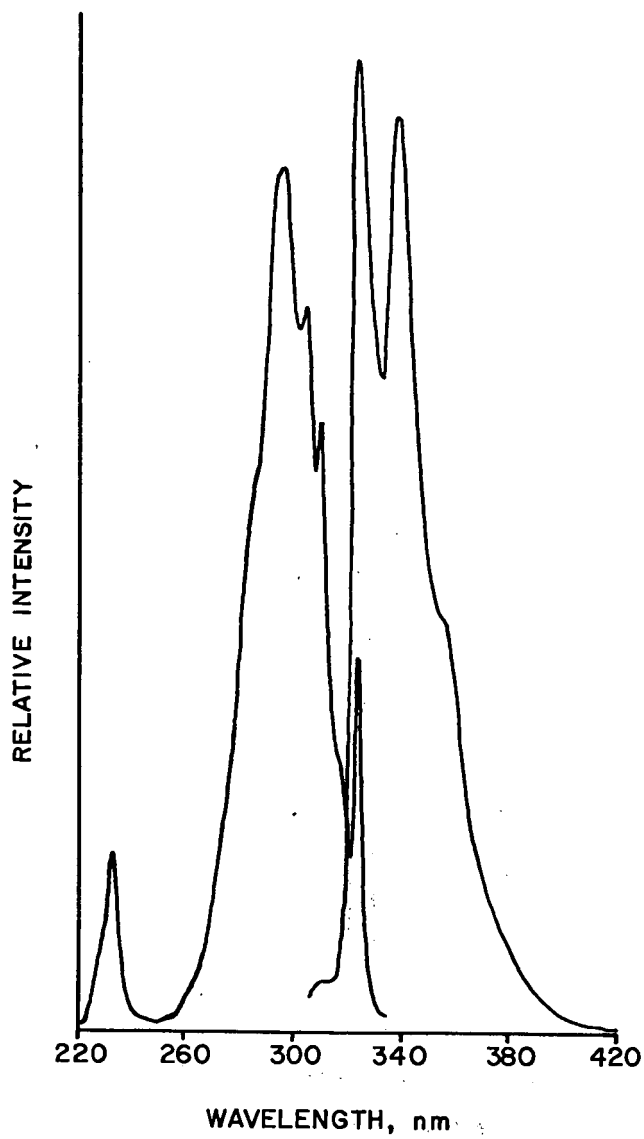
Figure 1

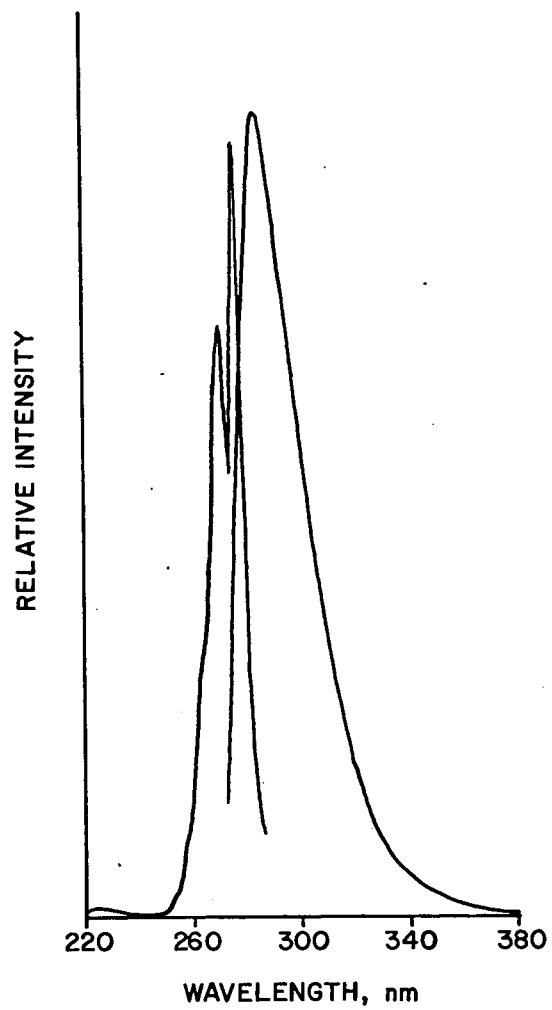


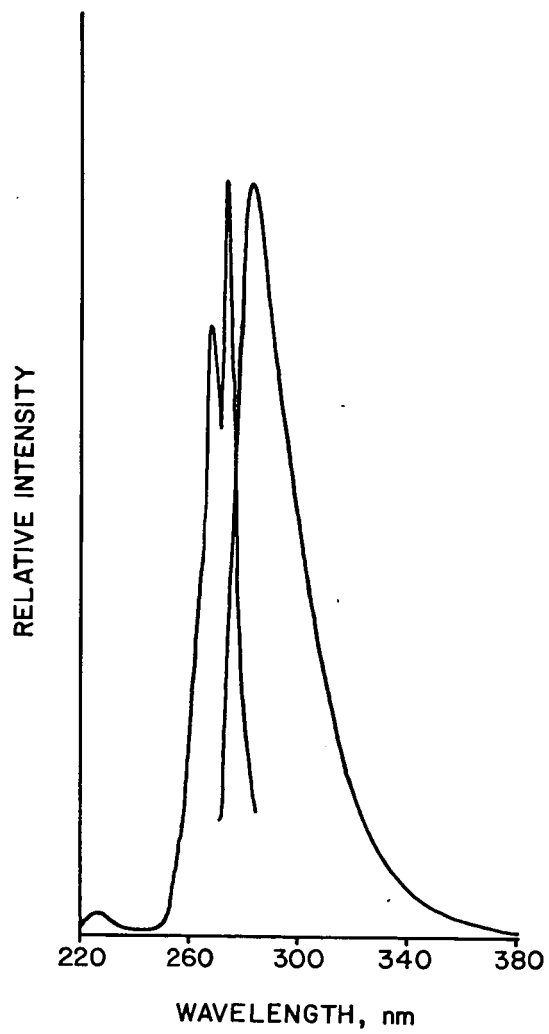


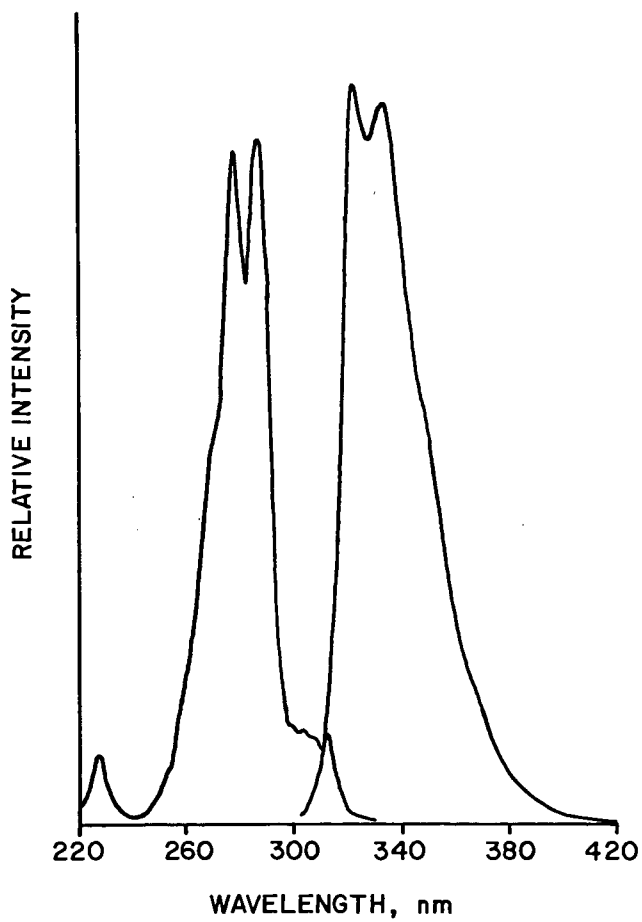


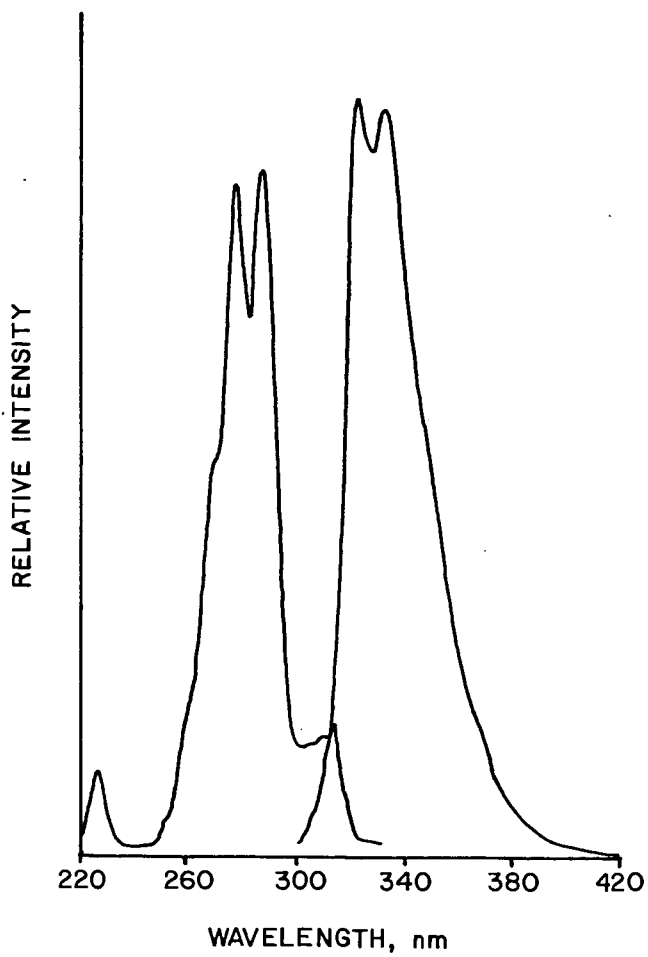


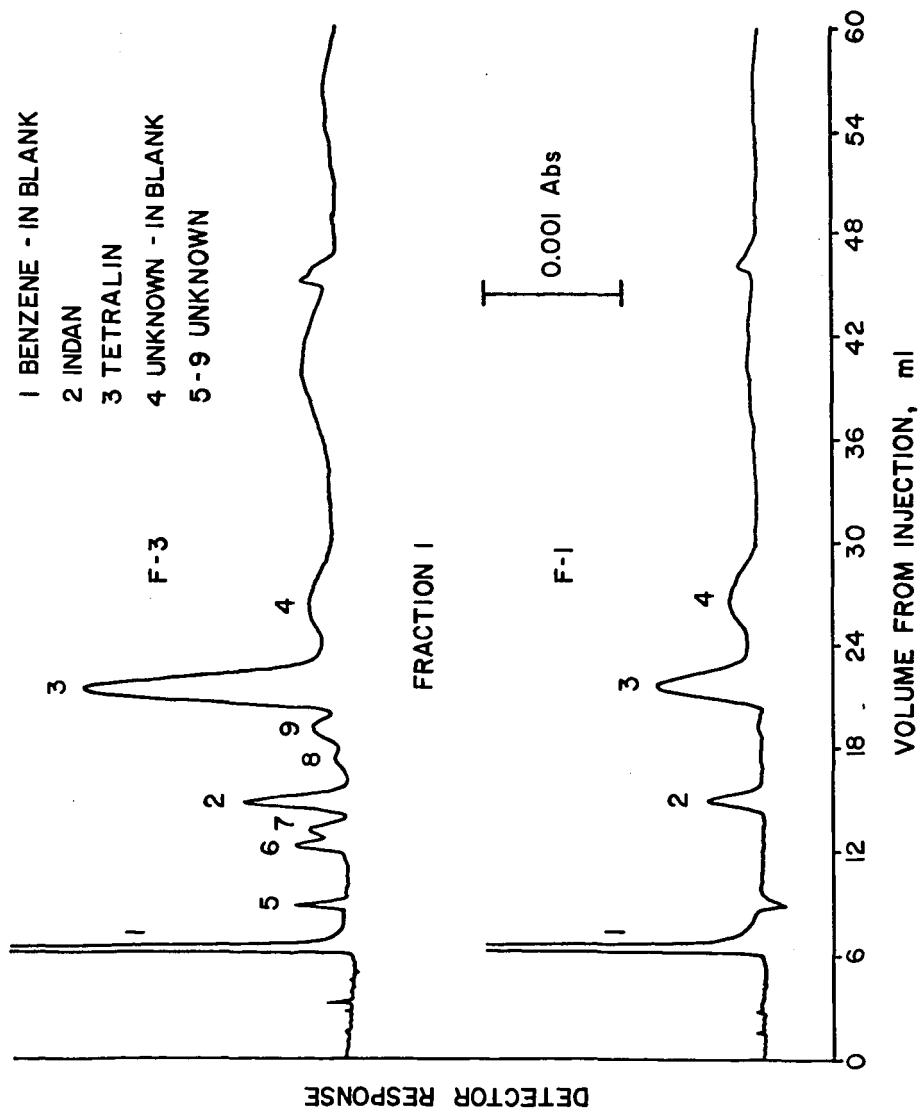


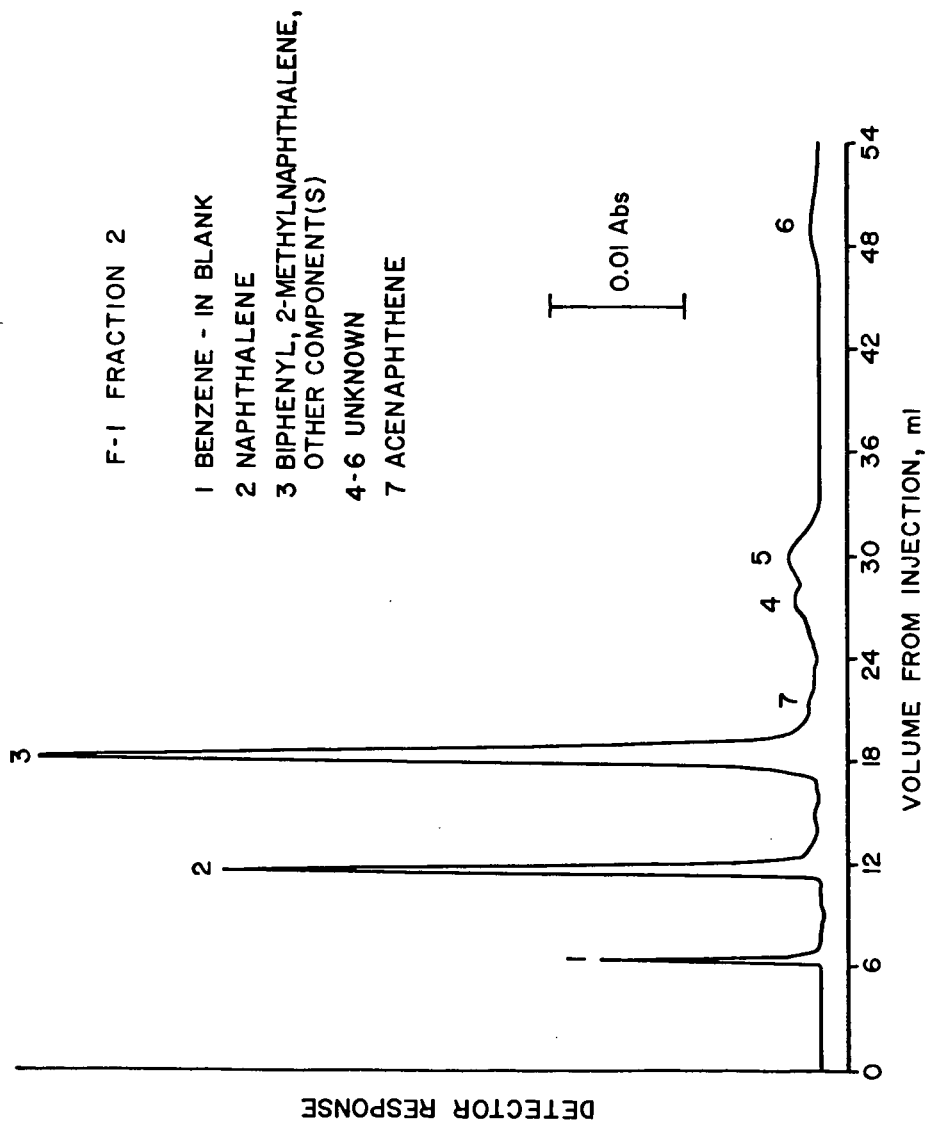












VISCOSITY OF COAL LIQUIDS - THE EFFECT OF CHARACTER
AND CONTENT OF THE NON-DISTILLABLE PORTION

by

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ABSTRACT

In coal liquefaction by direct hydrogenation, the objective of processes under study is to produce a liquid which might substitute for petroleum in fuel and refining applications. One difficulty with such coal liquids is the high viscosity exhibited by these materials at ambient temperature. This is especially important if the product were not to be fractionated by distillation but rather be filtered or centrifuged and transported by pipeline to be used directly as a boiler fuel. This report describes experimental work and conclusions concerning the effect of the heavy ends of coal liquids on the viscosity. In this work various distillation residues were dissolved in anthracene oil to produce a simulated coal liquid. The solvent was held constant for each of the residues studied; therefore, differences in the character of these distillation residues would cause the resulting solutions to be of varying viscosity. The character of the distillation residues was studied by high pressure liquid chromatography (HPLC) for molecular weight distribution, solubility in toluene and hexane, column chromatography, nonaqueous titration for weak acids and bases, elemental analyses for nitrogen and oxygen, and mass spectrometry using a solids probe inlet. Of these properties determined for the various solid residues, almost all were found to correlate with viscosity of the solutions. Molecular weight, oxygen content, concentration of weak acids, and hexane soluble constituents were most notable in correlating with solution viscosity. The mass spectral data, concentration of weak bases, and concentration of asphaltenes did not correlate with viscosity. It appears that hydrogen bonding is more important in defining the effect of asphaltenes and pre-asphaltenes on viscosity than are acid-base salt formation interactions. Of interest is the fact that in liquids where pre-asphaltenes are major constituents, the effect of asphaltene content is overridden. Pre-asphaltenes have a greater effect on increasing viscosity than do comparable concentrations of asphaltenes in coal liquids.

This work helps to define the problem to be overcome in producing low viscosity oil from coal without distillation of product. It appears to be absolutely critical to minimize the concentration of non-distillable materials in coal liquids as well as to reduce the molecular weight, acid content, and concentration of pre-asphaltenes in the oil. The effect of concentration of non-distillable material in a coal derived oil is dramatic; an increase from 20 pct non-distillable to 30 pct non-distillable for the oils studied increased the viscosity by a factor of approximately 30.

INTRODUCTION

At the Grand Forks Energy Research Center (GFERC) the CO-Steam process¹ for liquefaction of low-rank Western coals is being studied. This research was pioneered at the ERDA Pittsburgh Energy Research Center (PERC) where bench scale batch and continuous experiments were conducted. Work is in progress at GFERC to determine reaction kinetics, to evaluate process design, to optimize reactor configurations, and to characterize the liquid product in detail. One important result obtained thus far is that the molecular weight of the non-distillable portion of CO-Steam product is reduced rapidly at temperatures above 460° C. For these studies a one-liter batch autoclave is used and a 3-lb/hr continuous unit is under construction and will be operating in the near future. Product characterization is accomplished by a combination of analytical techniques including high resolution mass spectrometry, low voltage mass spectrometry² (LVMS), gas chromatography-mass spectrometry (GC/MS), high pressure liquid chromatography (HPLC) and column chromatography³.

In early product characterization work at GFERC, two CO-Steam product oils from PERC were encountered which had obviously different viscosities but essentially the same concentration of distillation residue (at 250° C and 1 torr). The volatile portions of the two liquids analyzed by LVMS and GC/MS showed the two distillates to be virtually identical as to the type and amount of the compounds present. It appeared that differences in viscosity of these two liquids was due to the character of the non-distillable portion. A program was then initiated to characterize properties of the distillation residue which might affect viscosity. The procedures to be described in the experimental section were applied to three distillation residues from coal liquefaction products (two CO-Steam liquids and a Synthoil liquid⁴) and to five solvent-refined coals⁵ (SRC's) which resemble the distillation residues of CO-Steam liquefaction products.

The viscosity of coal liquids and petroleum heavy ends has been the subject of some investigation, and the effect of the asphaltene content has been shown to be important in previous studies.⁶⁻⁸ Coal derived oils and petroleum oils which contained from 10 to 30 pct asphaltene showed a marked increase in viscosity with increasing concentrations of asphaltene. Removal of polar materials from a solid petroleum distillation residue gave saturate and aromatic fractions which were liquids.⁹ A paper by Burk and Kutta¹⁰ showed that molten asphaltenes exhibited a lower viscosity than do molten pre-asphaltenes at the same temperature. Solution viscosity of Athabasca asphaltene has been investigated by Moschopedis, et al.¹¹

One explanation for the marked increased in viscosity caused by asphaltene materials has been suggested to be acid-base interactions.⁶ Asphaltenes are polar compounds having hydroxyl, acidic nitrogen, and basic nitrogen groups. Possible acid-base interactions between hydroxyl or acidic nitrogen and basic nitrogen functions is thought to cause molecular aggregation. This would lead to very high resulting molecular weights and a corresponding trend toward highly viscous liquids. Data presented in this study, however, suggests that hydrogen bonding rather than acid-base interactions is responsible for the synergistic effect noted for asphaltene on viscosity. Because neither weak base content nor percent nitrogen correlate with viscosity, it appears that the content of weak base is not effective in defining molecular interactions among the asphaltene molecules.

EXPERIMENTAL

Materials Studied

The CO-Steam liquids and Synthoil liquid were obtained from the Pittsburgh Energy Research Center. Several grams of each liquid was distilled in a Kugelrohr oven at 250° C and 1 torr. The resulting distillation residue was removed and ground to minus 200 mesh for preparation of solutions. The solvent refined coals studied were obtained from Pittsburgh and Midway Coal Mining Co., Southern Services Inc., and the University of North Dakota (Project Lignite). Simulated coal liquids were made by dissolving 25 wt pct of the distillation residues or SRC's in anthracene oil. This concentration allowed differences in viscosity caused by various properties of the dissolved solids to be apparent and measurable. The viscosities were measured using a Brookfield viscometer, and the temperature of the liquids was held at 25.00 ± .03° C using a constant temperature bath while the viscosity was being measured. The solutions were prepared by warming and stirring a mixture of the powdered solid with anthracene oil for 16 hours. No undissolved solids were observed, and the log of viscosity was linear with concentration, showing that solution of the distillation residues or SRC's was complete.

Analytical Methods Used to Characterize Residues

Molecular Weight

The molecular weight of the residues was determined by dissolving the sample to 1 wt pct in tetrahydrofuran. Approximately 90 pct or more of each solid was soluble in tetrahydrofuran, so the value measured represented the molecular weight of virtually all of the sample. The one percent solution was injected into a Waters high pressure liquid chromatograph using 1-500 Angstrom and 3-100 Angstrom microstyragel columns which had been previously calibrated using the polystyrene standard supplied by Waters to measure molecular weight in the range encountered. Data were recorded using a strip chart recorder, and values for average molecular weight in the molecular weight ranges obtained are illustrated in Figure 1.

Content of Asphaltene and Pre-asphaltene

The distillation residues and SRC's were dissolved in a minimum quantity of tetrahydrofuran. Toluene was then added to produce a solution containing 95 pct toluene, thus precipitating the toluene-insoluble pre-asphaltenes. The toluene solution, containing the asphaltenes and oil, was filtered. The filtrate was then concentrated, and hexane was added to precipitate asphaltenes from a 95 pct hexane solution; asphaltenes were separated by filtration. The pre-asphaltene, asphaltene, and hexane soluble oil were measured by determining the weight of each fraction separated from the original solid.

Column chromatography using alumina and a gradient elution approach³ was used to determine the concentration of hydrocarbons plus ethers contained in the distillation residue and SRC. The sample of solid to be analyzed was preadsorbed on neutral alumina and added to a column containing alumina. Toluene was passed through the column and the hydrocarbons plus ethers were collected. The toluene was evaporated and the weight of material eluted was measured. The content of hexane soluble oil, as well as hydrocarbon plus ether compounds in the sample, were found to correlate with viscosity. Data are summarized in Table 1 for the concentration of asphaltene, pre-asphaltene, hexane soluble oil, and non-polar compounds in the solids studied.

Non-aqueous Titration for Acid and Bases

The solids to be analyzed for acids were weighed to give approximately 0.4 grams of the solid; this was then dissolved in 50 ml of pyridine and protected from atmospheric carbon dioxide using nitrogen. The sample was titrated with tetrabutyl ammonium hydroxide in methanol/benzene as solvent using a glass versus methanol modified calomel electrode system. Data were recorded using a strip chart recorder. Weak bases were determined in an analogous way except that the titrant was perchloric acid in dioxane and the titration medium was 9:1 tetrahydrofuran/acetic acid.

Elemental Analysis

Nitrogen was determined using the Kjeldahl method and oxygen was measured by neutron activation analysis. The activation analysis was performed by Intelcom Rad. Tech., San Diego, CA.

Mass Spectrometry of Residues

The solids to be analyzed by mass spectrometry were placed in weighed one millimeter sample tubes and introduced into the solids probe inlet of a DuPont 21-491B low resolution mass spectrometer. The solids probe was heated to 200° and a mass spectrum of the vaporized material was obtained. After heating for several minutes at 200° no further vaporization of samples was evidenced by the absence of peaks in the mass spectrum. The capillary tube was removed and weighed to determine the quantity of material vaporized.

After weighing, the capillary tube was put back into the mass spectrometer and heated to 350° where another spectrum of the volatile material was recorded. After 350° heating for several minutes (to the point where no further sample vaporized) the capillary tube was removed from the mass spectrometer inlet and weighed to determine the total quantity of material vaporized. Approximately 1 milligram samples were used, and a Cahn Model 4700 electrobalance was employed for determining weight changes.

RESULTS AND DISCUSSION

Effective Concentration of Residue

The change in viscosity with concentration of residue in the simulated coal liquids is most dramatic for three different residues dissolved in anthracene oil in the range of 20-30 pct concentration. Figure 2 shows that the viscosity of the resulting solution can be increased by a factor of 20-40 for a 50 pct (relative) change in concentration of residue. Reducing the concentration of residue is perhaps the most important property to be influenced by changes in process variables. To make a product with a low concentration of residue is a first objective, and then liquefaction conditions might be changed so as to give non-distillable material which will minimize viscosity of the resulting coal liquid.

Properties of Residues Which Correlate with Viscosity

The relationship between non-polar content and log viscosity is illustrated in figure 3. Both the percent soluble in hexane and the saturates plus aromatics obtained by elution in the column chromatography is shown to be a linear plot with a negative slope, indicating that the greater the concentration of hexane soluble material in the distillation residue, the lower will be the viscosity. Inversely, figure 4 shows a plot of pre-asphaltene content and percent of polar and polymeric material versus log viscosity. Again a reasonable correlation is seen. The asphaltene content related to viscosity shows somewhat random distribution. This is true because all of the residues studied have a significant content of pre-asphaltenes, and the effect of the asphaltenes is somewhat overridden by this large concentration of more effective viscosity-increasing constituents.

Data obtained previously by Sternberg et al⁴ for variations of viscosity of Synthoil products with asphaltene content can be explained in terms of these results. When their data is replotted as log of viscosity versus percent asphaltene, the relationship is linear in the range of 5-20 pct asphaltenes; however, Synthoil liquids having from 20-40 pct asphaltenes show a positive deviation from linearity with log viscosity versus percent asphaltene. This positive deviation illustrates the effect of the pre-asphaltenes in those Synthoil liquids having high asphaltene content. Those materials with high asphaltene would have correspondingly more pre-asphaltene, and it is more effective in raising viscosity than is asphaltene.

The correlation of molecular weight with log viscosity is also linear and is illustrated in figure 5. When the average molecular weight of the distillation residues varied over the range of 290 to 500, the resulting solution's viscosity changed by a factor of 15. The material of molecular weight greater than 750 in the molecular weight distributions (Figure 1) may be the most important contributor to the increase in viscosity. These high molecular weight species in particular could lead to pronounced viscosity increases as was noted for pre-asphaltenes.

Examination of the distillation residues and SRC's directly by mass spectrometry did not yield very useful data. Only 10 to 25 pct of the SRC or residue was volatile in the mass spectrometer inlet, and no clear correlation could be drawn.

The variation of viscosity with both oxygen content and weak acid content is illustrated in figure 6. Molecular weight, weak acid content, and oxygen content of the non-distillable portion of coal liquids are all reduced by more severe reaction conditions, and this brings about an accompanying decrease in viscosity. It is not clear which of these properties are most important in defining the viscosity of the resulting liquid. Both molecular weight and concentration of polar groups could be important, and at this time, the data does not show which of these two parameters is predominant.

Of particular note, however, is that the weak base content and the percent nitrogen does not correlate with viscosity. Thus, the suggestion that acid-base interactions are responsible for highly viscous solutions of asphaltenes does not appear to be supported by this data. If both weak acids and weak bases were important, then viscosity should increase with the concentration of both. However, only acids appear to be definitive in establishing the viscosity. The conclusion which may be drawn is that hydrogen bonding of the hydroxyl groups and acidic nitrogen groups is of major importance while acid-base interactions are of lesser importance.

The various properties that have been shown to correlate directly with log viscosity are molecular weight, oxygen content, content of pre-asphaltene, and weak acid content. An inverse correlation is seen with the hexane solubility and saturates plus aromatics in the distillation residue. In a coal liquefaction process, all of these parameters will change in the direction of a lower viscosity product in a somewhat simultaneous way. It is not known at this point if one of these properties of the heavy ends would be more advantageously reduced during coal liquefaction than any of the other parameters studied. It can be safely stated, however, that decreasing the concentration of the non-distillable material in the coal liquid is absolutely necessary in lowering the viscosity of the product. Concurrent with this, improvement of the properties of this distillation residue tends to occur automatically. Further work is needed to define the changes in process variables which might bring about a reduction in undesirable properties of the distillation residue.

ACKNOWLEDGMENT

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TABLE 1. - Viscosity, molecular weight, and solubility

	Solution viscosity ^{c/} (centipoises)	Wt. Avg. molecular weight HPLC	Weight percent		
			Hexane solubles	Asphaltenes	Preasphaltenes
Synthoil residue.....	400	340	50.3	26.5	23.2
SRC 115.....	560	295	51.7	24.0	24.3
CO-Steam I residue ^{a/} ...	1552	450	24.2	12.3	63.5
CO-Steam II residue ^{b/} ...	1667	395	31.8	28.1	40.1
SRC Pitt 8....	1774	420	26.2	20.6	53.2
SRL M5C.....	1945	415	24.6	7.8	70.5
SRC 308.....	4467	495	15.6	14.4	70.0
SRC 122.....	6223	550	20.9	14.6	64.5

^{a/} Tubular reactor.^{b/} Stirred autoclave.^{c/} Viscosity of 25 pct (w/w) solution in anthracene oil at 25° C.

TABLE 2. - Column chromatographic separation

	Weight percent per fraction				
	Toluene	Chloroform(1)	Chloroform(2)	THF ethanol	Uneluted
	1	2	3	4	5
Synthoil residue.....	15.9	1.7	37.6	40.0	4.8
SRC 115R.....	30.9	4.5	30.3	31.9	2.4
CO-Steam I residue ^{a/} ...	14.0	4.0	9.8	36.7	35.5
CO-Steam II residue ^{b/} ...	19.2	2.8	19.9	51.3	6.8
SRC Pitt 8....	13.5	3.8	14.7	63.2	4.8
SRL M5C.....	13.4	1.6	4.1	41.4	39.5
SRC 308.....	8.1	1.7	16.7	48.1	25.4
SRC 122.....	9.1	2.0	14.4	54.3	20.2

a/ Tubular reactor.

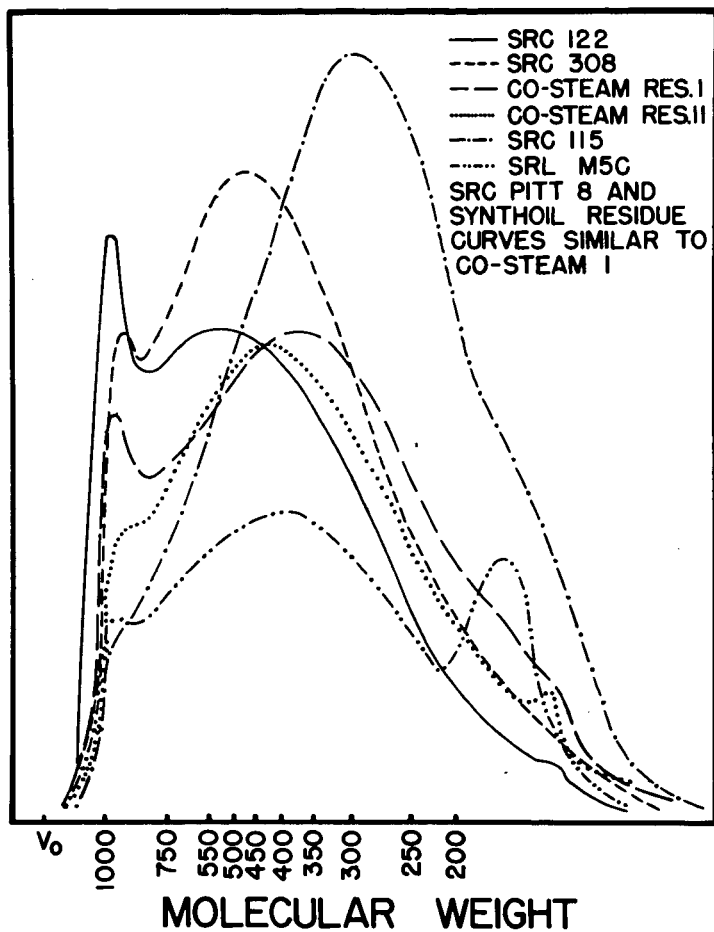
b/ Stirred autoclave.

TABLE 3. - Acid and base content

	Acidity meg H ⁺ /g	Pct oxygen, neutron activation	Basicity meg OH ⁻ /g	Pct N, Kjeldahl
Synthoil residue.....	2.066	---	0.750	---
SRC 115.....	1.481	1.55	0.711	1.70
CO-Steam I residue ^a /.....	1.661	7.03 ^c /	0.449	1.15
CO-Steam II residue ^b /.....	1.938	3.72	0.476	1.23
SRC Pitt 8.....	2.019	3.56	0.647	---
SRL M5C.....	2.060	---	0.522	---
SRC 308.....	2.285	4.32	0.786	1.78
SRC 122.....	2.531	4.69	0.713	1.55

^a/ Tubular reactor.^b/ Stirred autoclave.^c/ Contains ash, inorganic oxygen present.

FIGURE 1



**MOLECULAR WEIGHT DISTRIBUTIONS OF SRC'S
 AND RESIDUES BY GEL PERMEATION HIGH
 PRESSURE LIQUID CHROMATOGRAPHY**

FIGURE 2

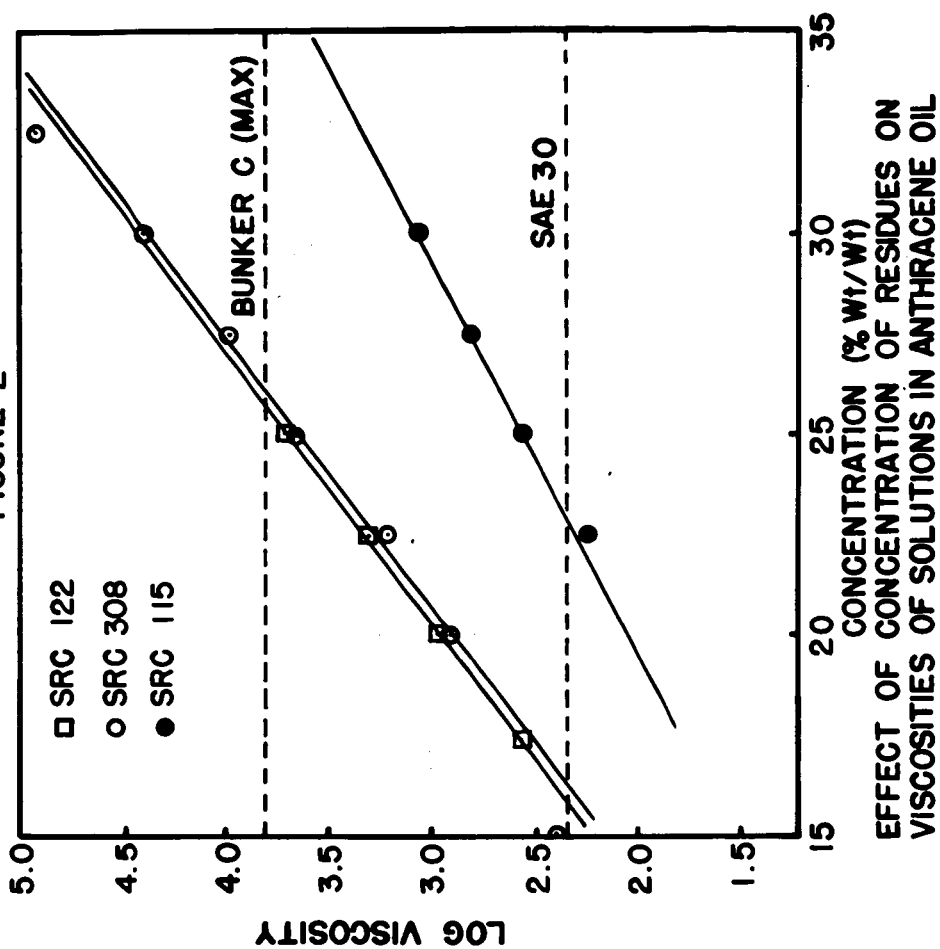
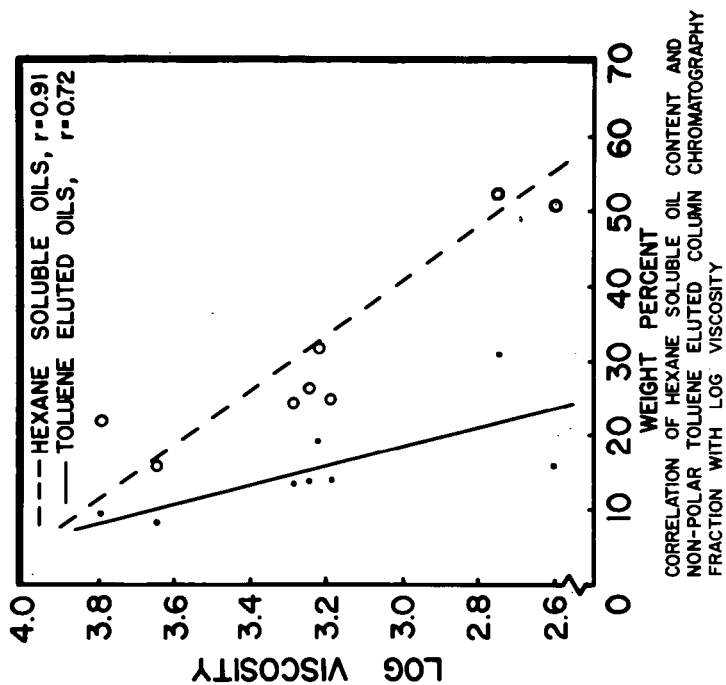


FIGURE 3



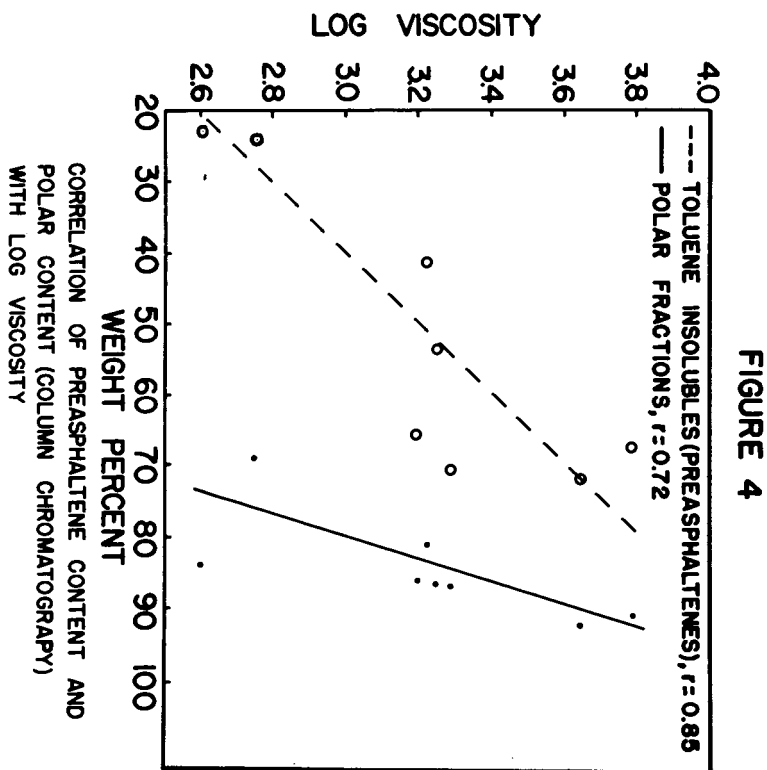


FIGURE 5

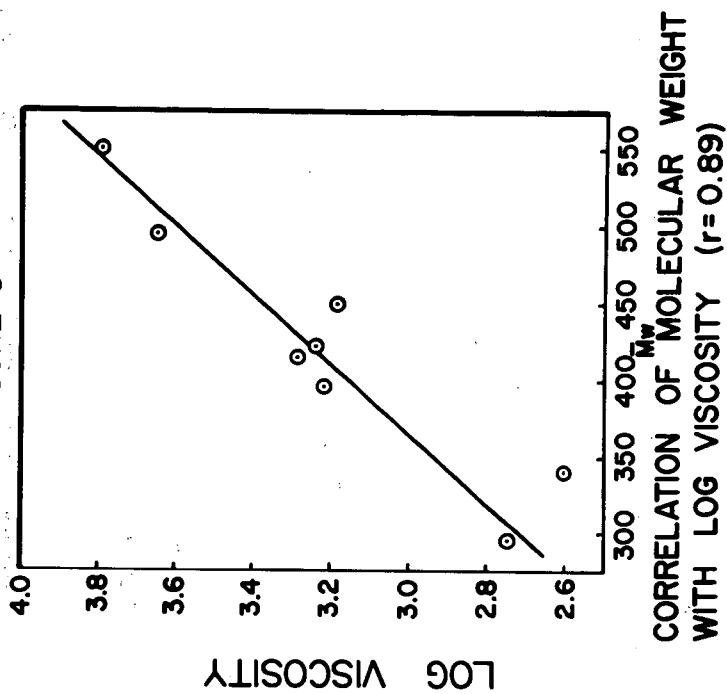
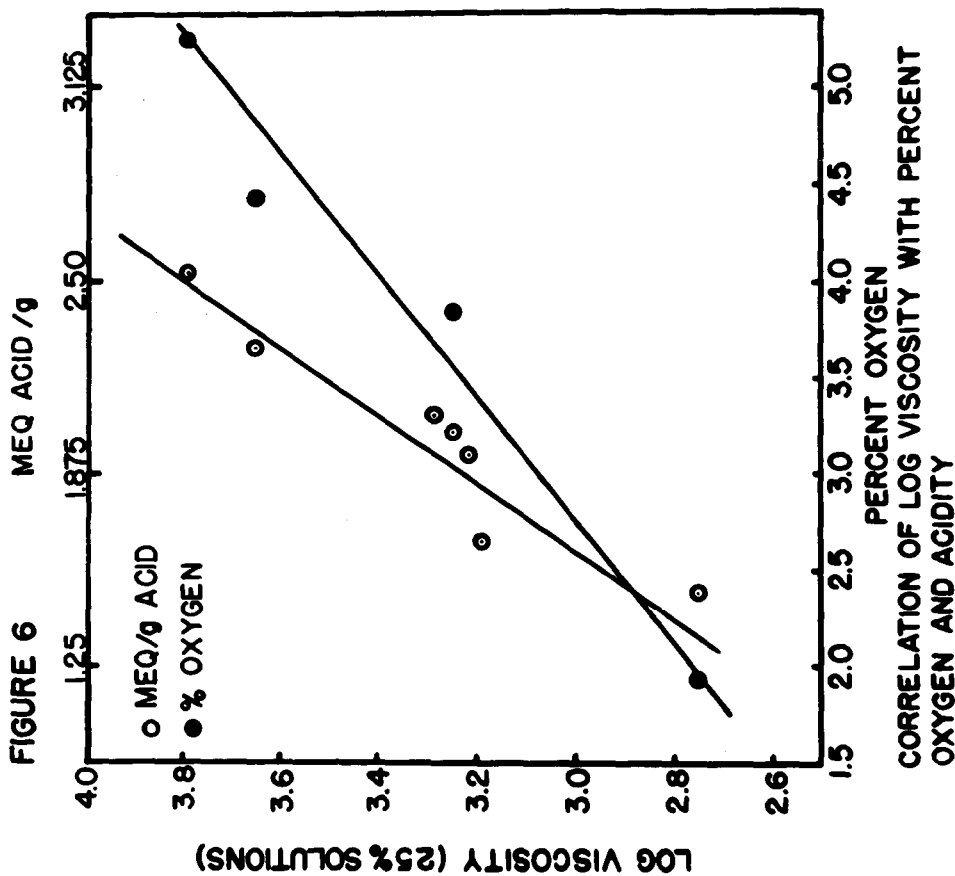


FIGURE 6



TEMPERATURE EFFECTS ON COAL LIQUEFACTION; RATES OF DEPOLYMERIZATION
AND PRODUCT QUALITY AS DETERMINED BY GEL PERMEATION CHROMATOGRAPHY

by

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INTRODUCTION

In this paper the reactor temperature and residence time effects on the depolymerization of coal will be discussed. The ratio of the absorbances of the 950 molecular weight (MW) to 280 MW peaks observed in the gel permeation high pressure liquid chromatography (HPLC) separation of products has indicated use as a measure of depolymerization and product quality.

Research on the non-catalytic CO-Steam liquefaction of coal was initiated at the Grand Forks Energy Research Center (GFERC) in 1974 as a continuation of research started at the Pittsburgh Energy Research Center (PERC). The objective is to develop the process as a commercial, economic method to produce a stable coal liquid which will meet environmental requirements (ash, nitrogen, and sulfur contents) for use as a boiler fuel. The research program has followed three overlapping stages: 1) Batch autoclave research, 2) 3-lb/hr continuous process unit operation, and 3) process development unit scaleup based on findings from (1) and (2). Selected data from item (1) will be considered in this paper.

The batch autoclave consists of a batch reactor system that can be charged with room temperature slurry to a hot (up to 500° C) reactor which can be sampled (both liquid and gas phases) at various times to determine reactant and product changes. Figure 1 depicts the fractions that are obtained during analysis. This system is also being utilized to determine total gas content of slurry at up to 4500 psig and 480° C. The amount of the material charged that is found in the gas phase in the reactor at various temperatures and pressures has been determined, and the effects of slow (1 hour) or rapid (3 minute) heatup of slurries to reaction temperature on molecular weight distributions and coking is being studied.

Undistilled coal products (solvent refined coals and coal liquids) analyzed at GFERC have contained 10 to 80 pct volatiles at 1 torr and 250° C. This volatile material is readily analyzed by GC, GC-MS, or low voltage MS. Approximately 50 to 80 pct of the non-volatile fraction was readily soluble in tetrahydrofuran (THF). Analysis of a 1 w/w pct solution of this non-volatile fraction (after passing through a 0.5 μ filter) has yielded molecular weight distributions which are not masked by solvent or light organic material. The technique has enabled the determination of the rate of disappearance of high molecular weight materials as a function of reactor temperature and residence time.

EXPERIMENTAL

Gas-Slurry Charge Composition

The one-liter reactor was typically charged with 250 gms of slurry (from a cylinder to the reactor using gas pressure). The amount of gas charged was approximately 3.5 moles. Molecular weight distributions have been found to be essentially independent of whether the charge gas was CO or synthesis gas (50:50 hydrogen to carbon monoxide). For the data reported, 250 gms of slurry were charged. The slurry composition was as follows:

27.3% as-received coal
8.0% of water added
58.2% anthracene oil
6.5% tetralin

Proximate and ultimate analysis for the lignite used in these studies is presented in Table 1.

TABLE 1. - Beulah Standard 2; GF 77-712

	Coal (As received)	Coal (Moisture free)	Coal (Moisture and ash free)
Proximate analysis, pct:			
Moisture.....	27.80	--	--
Volatile matter.....	30.45	42.18	46.93
Fixed carbon.....	34.45	47.71	53.07
Ash.....	7.30	10.11	--
TOTAL	100.00	100.00	100.00
Ultimate analysis, pct:			
Hydrogen.....	6.09	4.16	4.63
Carbon.....	46.30	64.14	71.35
Nitrogen.....	0.72	1.00	1.11
Oxygen.....	39.03	19.82	22.05
Sulphur.....	0.56	0.77	0.86
Ash.....	7.30	10.11	--
TOTAL	100.00	100.00	100.00

Molecular Weight Distribution Determinations

The equipment used to determine molecular weight distributions was a Waters Model ALC-GPC-201 system fitted with one 500 and three 100 Å microstysragel columns. CO-Steam product samples were first distilled at 250° C and 1 torr to remove volatile material. A 1 w/w pct tetrahydrofuran (THF) solution of

the non-distillable material was passed through a 0.5μ filter prior to injection. The percent THF insoluble residue was compared to THF solubility data obtained for a sample that was not subjected to distillation. A quotient of stability to distillation can be calculated which reflects the fraction of the original THF soluble material that was still soluble after distillation at 250°C and 1 torr. This stability quotient has been found to increase with reactor residence time and temperature.

In run 30, the reactor was charged cold and heated to $400 \pm 2^\circ \text{C}$ in 92 minutes and held at this temperature for 1/2 hour. The reactor was subsequently heated to and held in steps at $435 \pm 4^\circ \text{C}$ and $475 \pm 5^\circ \text{C}$.

In Table 2, data from run 30 are presented. The stability quotient increased from 22 to 56 pct in 19 minutes at 400°C . In going to 437°C the quotient goes to 71 pct and for the next 104 minutes remained essentially constant. The stability quotient also reflects the quantity of sample that is analyzed by HPLC after distillation.

TABLE 2. - Product stability to distillation versus residence time and temperature in run 30

Sample No.	Temp., $^\circ \text{C}$	Time	Product fractions		Stability quotient, pct ^{b/}
			(1) THF Insoluble, pct ^{a/}	(2) Non-distillable, pct ^{a/}	
1 3	$400^\circ \pm 2^\circ$	92			
		94	11	22	22
		113	6	18	56
4 6	$435^\circ \pm 4^\circ$	141			
		142	7	22	71
		182	9	20	78
7 9	$475^\circ \pm 5^\circ$	200			
		212	8	23	74
		246	11	29	73

a/ The values for (1) and (2) are percents of total reactor slurry product obtained at reactor temperature and pressure.

b/ The stability quotient is the percent of (2) minus (1) that was soluble after distillation at 250°C and 1 mm Hg.

The molecular weight distributions were measured relative to commercially available standards (purchased from Waters) to enable comparison by other researchers. Detection was by UV at 254 nm.

RESULTS AND DISCUSSION

The temperature at which the reactor was operated has had dramatic effects on the molecular weight distribution obtained for the non-distillable, THF soluble fraction of coal liquefaction products.

Figure 2 depicts the molecular weight distributions obtained at 400, 435 to 450, and 460 to 480° C for residence times under 1/2 hour. These distributions have been observed in experiments where the reactor was heated to temperature in 3 minutes or in 1 hour. Figure 2 illustrates the rapid decrease in the absorbance at molecular weights greater than 750 and the shift of the average molecular weight of this fraction from over 600 at 400° C to about 500 at 440-450° C and finally to about 300 at 460 to 480° C. Since the absorbance is proportional to concentration, ratios of the absorbance maximum between 1200 and 950 to the value at 280 MW (A_{950}/A_{280}) have been used to correlate data from various experiments. This ratio has also been found to be independent of experimental errors in preparing 1 w/w pct solutions. In Figure 3, the ratios obtained for samples removed for under 1/2 hour residence times during 1/2 hour residence time for a number of experiments are depicted versus reactor temperature.

High ratios indicate large concentrations of over 750 MW molecular weight material. The rapid decrease of the ratio with temperature indicates that reactors operated at higher temperatures produce products with lower average molecular weights.

Rates of Depolymerization

The change in molecular weight distribution with reactor residence time can be used as a qualitative measure of the rates of depolymerization at different temperatures. At 400° C the molecular weight distribution changes little with time (Fig. 2). However, the stability to distillation does increase, (Table 2) which indicates that the quality of the product increases with residence time. Change in product at 400° C have not been studied to any degree since the molecular distribution observed is similar to that of solvent refined coals, which are not liquids at room temperature.

At temperatures of 435 to 450° C notable residence time effects have been observed especially in the greater than 750 MW material. Figure 4 presents two ratios (A_{950}/A_{250} and A_{450}/A_{280}) versus residence time for an extended experiment in which the reactants were initially heated to 440° C in three minutes and held there for 1/2 hour, followed by stepwise heating during 5-10 minutes and holding for 1/2 hour at 450, 460, and 470° C. After 30 minutes at 440° C, the ratio A_{950}/A_{250} tends to level off. The changes observed were on similar fractions of total product. The molecular weight distribution and the ratios observed at 440° C were similar to those observed for CO-Steam product prepared at PERC.

A rapid decrease in the A_{950}/A_{280} ratio occurred within 7 minutes of heating from 440° to 450° C. Additional time at 450° C yielded little change in the ratio. The A_{450}/A_{280} ratio also leveled off. Molecular weight distributions for this material indicated that no recoverable material greater than 1000 MW was present; however, the distribution did have a shoulder at 950 MW. These results are similar to those obtained for coal liquids produced by the Synthoil Process.

Subsequent heating to 460° C caused an additional decrease in both the A_{950}/A_{280} and A_{460}/A_{280} ratios, with little change continuing after 15 minutes. Little further change has been observed in these molecular weight distributions in other experiments at 470° C for 1 hour or at 480° C for 1/2 hour. Similar distributions have been obtained for samples made by the SRC II Process.

The most dramatic decrease in molecular weight occurred during heating from 440 to 450° C. However a further beneficial decrease occurs between 450 to 470° C. Depolymerization occurs very rapidly at 460° C, and the 300 MW material produced does not depolymerize further with time beyond 15 minutes.

Product Quality

Other research being conducted at GFERC has indicated that there is direct dependence of viscosity on the average molecular weight and the concentration of pre-asphaltene material.¹ Asphaltene content in higher concentrations has also effected increased viscosities of coal products.^{2,3,4} Figure 5 depicts the molecular weight distributions of pre-asphaltene and asphaltene fractions obtained from PERC CO-Steam, SRC II, and the GFERC product produced at 470° C. For each product, the asphaltene fraction has a lower average molecular weight than the pre-asphaltene fraction. Absorbance at 950 MW is most indicative of the presence of the higher MW pre-asphaltene and asphaltene material, and that at 280 MW of lighter non-distillable material.

The A_{950}/A_{280} ratio should correlate well with the viscosity for a totally coal derived product. The A_{460}/A_{280} ratio should be useful as a measure of product quality after the absorbance at 950 MW approaches zero.

ACKNOWLEDGEMENTS

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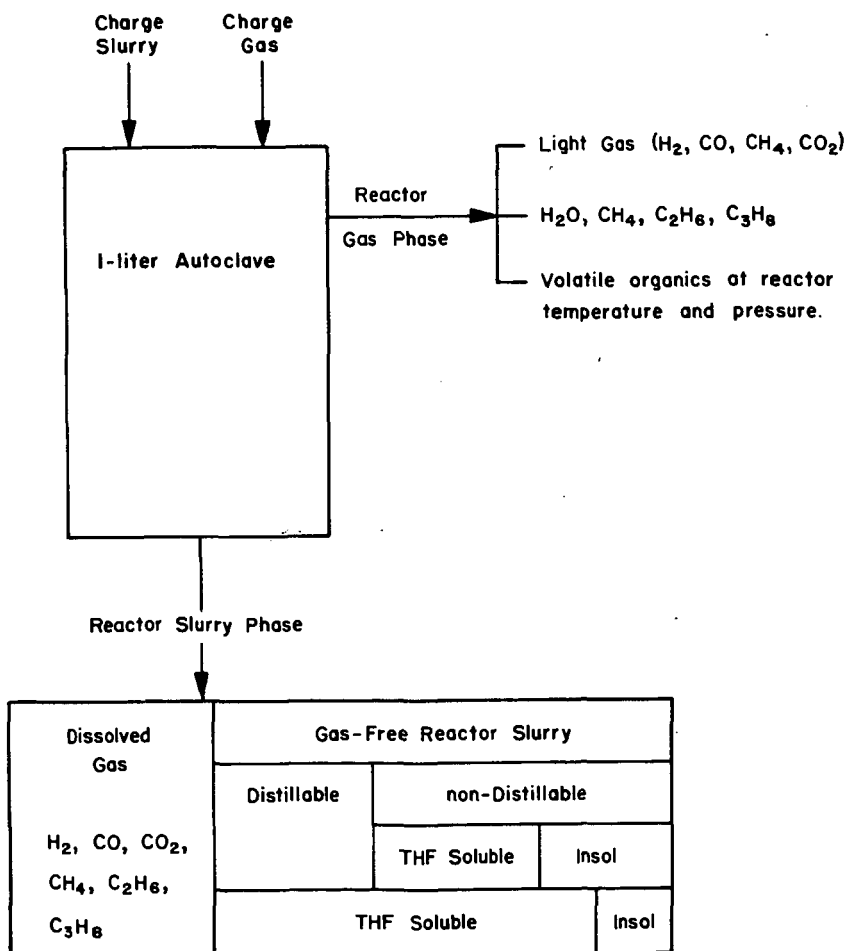


FIGURE 1. - Major sample fractions derived from batch autoclave studies on CO-Steam kinetics.

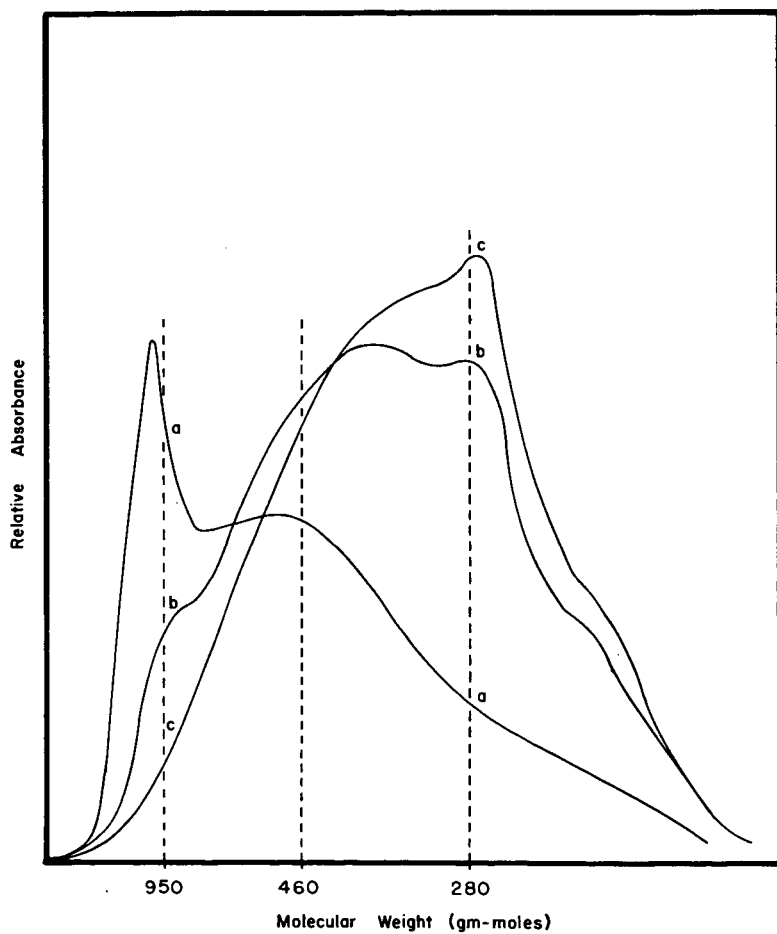


FIGURE 2. - Average MW distributions obtained at a) 400° C, b) 440-460° C, and c) 460-480° C for the non-distillable, THF soluble fractions of coal liquid products.

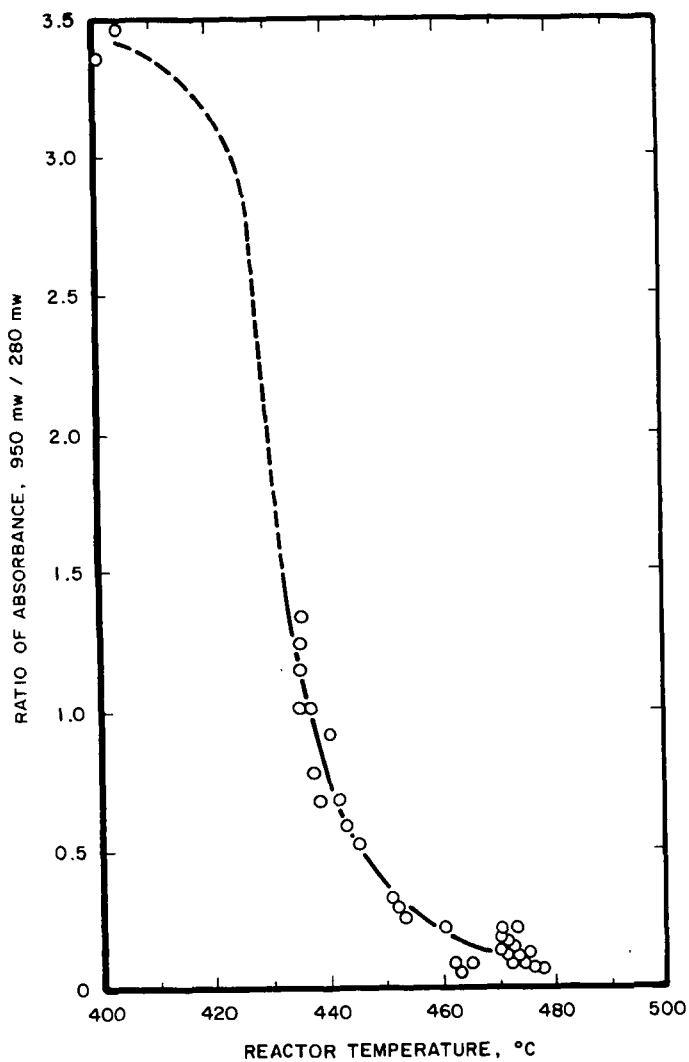


FIGURE 3. - Correlation of the A_{950}/A_{280} ratio to reactor temperatures for residence times under one-half hour.

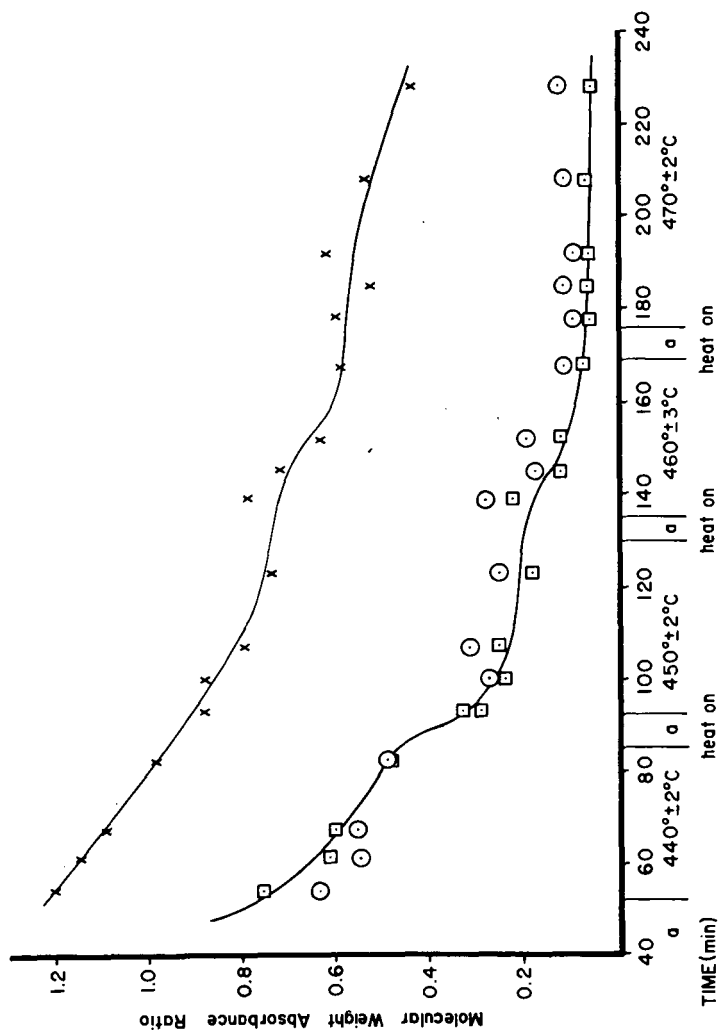


FIGURE 4. - Molecular weight absorbance ratios versus time at various temperatures. (A950/A280 = □; A460/A280 = ○) During time interval "a" the temperature is increasing.

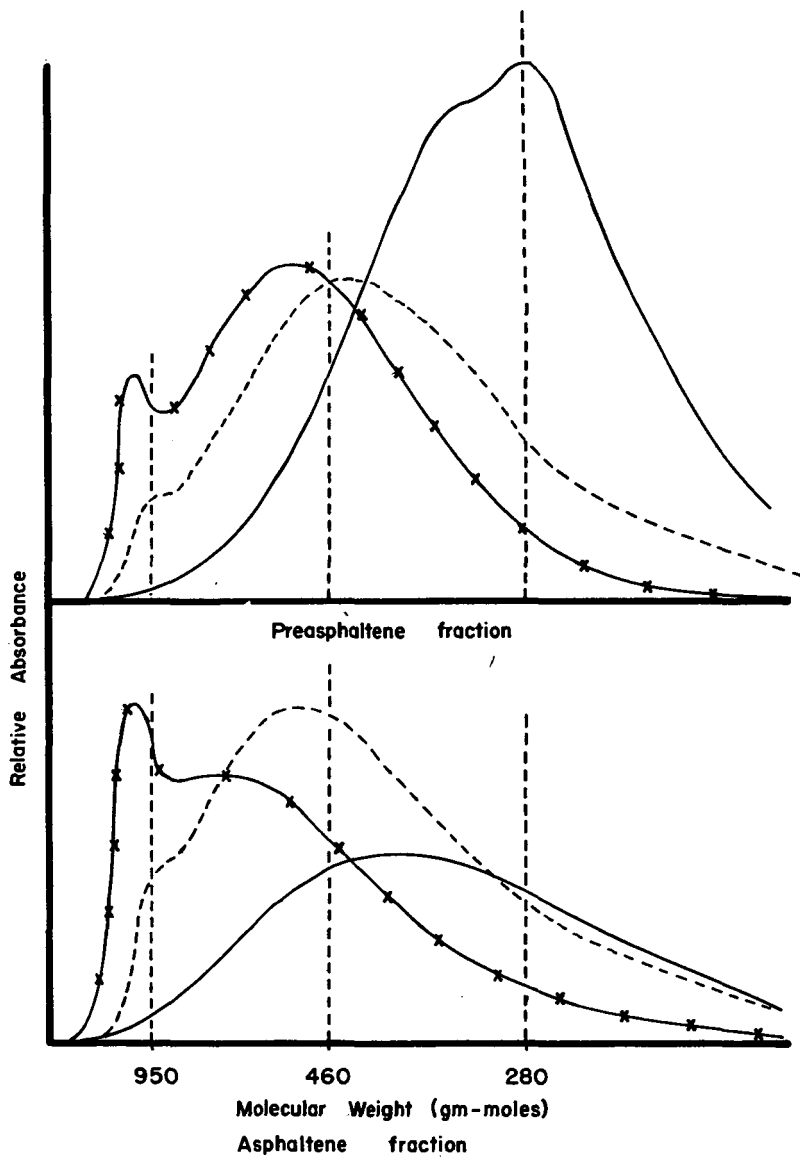


FIGURE 5. - Comparison of molecular weight distributions for coal liquid fractions obtained from PERC CO-Steam (x-x), SRC II (----) and GFERC, 470° C (—) samples.

INDIRECT MEASUREMENT OF SEDIMENTATION RATES AT HIGH TEMPERATURE AND PRESSURE BY X-RAY PHOTOGRAPHY

by

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ABSTRACT

A settling column has been developed which can be used in conjunction with x-rays to follow the settling of mineral particles in opaque liquid at high temperatures and pressures. The mineral particles attenuate the x-rays to a much greater extent than the liquid. This indirect x-ray system produces photographs showing the solids settling front as a function of height at a given time without disturbing the sedimentation process.

This system consists of a x-ray head and a special steel settling chamber with aluminum windows, placed in a lead lined box. The cell is connected to an autoclave from which the sample is transferred after preparation. This system is capable of run temperatures up to 315°C and pressures up to 2.9×10^6 N/m². Data are reported for the sedimentation of mineral particles in a coal liquid with and without the addition of solvent. The experiments are reproducible to within 10% error. The x-ray measurement technique provides both the initial settling rate and the height of the compression region.

INTRODUCTION

In the coal liquefaction process some coal particles and mineral matter are not converted to the liquid product. To utilize this product as a fuel, the solids must be eliminated. Many processes for solids removal are being investigated, such as filtration, centrifugation and solvent precipitation. Solvent precipitation has been studied in detail by various research groups in determining the settling properties of the particles. Continental Coal Development Corporation (Gorin, et al., 1975; Burke, 1976), Argonne National Laboratories (Huang and Fischer, 19) and Oak Ridge Laboratories (Rodgers, 1975, 1976) employ direct sampling techniques to determine the solids concentration as a function of time and/or height in sedimentation columns. This procedure is very time consuming because of the number of chemical analyses which must be performed. In addition the sampling disrupts the settling phenomena to some extent. The indirect x-ray technique avoids the direct sampling problem and permits rapid measurement so that a wide range of chemical additives can be screened.

There are numerous techniques to measure the initial settling rate of solids in clear or translucent liquids. Most of the common light absorption or light scattering techniques cannot be used in opaque solu-

tions. X-rays have been used through the years in the medical field as well as in industry. X-rays have been previously employed to determine particle size distribution via sedimentation. The Sedigraph 5000 is one such instrument, manufactured by Micromeritics Instrument Corporation, that measures particle size distribution from settling rate data by detecting the concentration of particles remaining at decreasing sedimentation depths as a function of time at room temperature and pressure. This apparatus could not be used for the conditions of sedimentation for coal liquids because of the high pressures and temperatures.

This paper discusses an x-ray system which was devised to meet severe process conditions. In general the apparatus involved an autoclave for the preparation of the sample and the settling chamber for x-ray detection of the settling solids. Most parts were made of steel with aluminum windows for x-ray penetration. Sedimentation can be determined over a range of temperatures (ambient to 315°C) and pressures (atmospheric to 2.9×10^6 N/m².)

The coal liquid used in the experiments that follow is Solvent Refined Coal (SRC) filter feed. Mineral matter content of SRC filter feed is within a range of 2.6 to 3.0 wt.% from low temperature ash studies. The SRC filter feed used is in a 3/1 ratio of solvent to coal.

EQUIPMENT

The sedimentation cell is shown in a schematic in Figure 1. The steel parts of the cell are extremely over designed. The thin aluminum windows are of different thickness for the different pressures. Presently, 0.16 cm thick windows are used in all experiments with a maximum pressure of 1.1×10^6 N/m². The x-rays penetrate the thickest windows (0.25 cm) which are required for the maximum pressure of 2.9×10^6 N/m². Garlock gaskets are used to make a seal between the aluminum windows and the steel body of the cell with the aid of sealing compound. The dimensions of interest are given in Figure 1. The volume of the cell is 80 cm³.

The schematic of the apparatus is shown in Figure 2. The settling chamber is placed in a lead lined box and is connected through the box to a 300 ml Parr Instruments Autoclave. High pressure and temperature filter holders as well as the solvent tank and settling chamber are connected to the autoclave with stainless steel tubing and high temperature Hoke valves (0.79 cm orifice). The autoclave has a temperature controlled heating mantle for constant temperature from ambient to 400°C and an electric motor which produces a continuous range of speeds from zero to 1000 rpm. The stirrer is water cooled when run at elevated temperatures. A corrosion resistant pressure gauge (0 to 2.9×10^6 N/m²) is used on both the autoclave and the settling chamber.

The settling chamber is heated externally with heating tape and the temperature is sensed by four type K thermocouples, in the body of the cell, connected to a multi-point temperature recorder. The cell with the heating tape and thermocouples is insulated such that there is no obstruction to the aluminum windows.

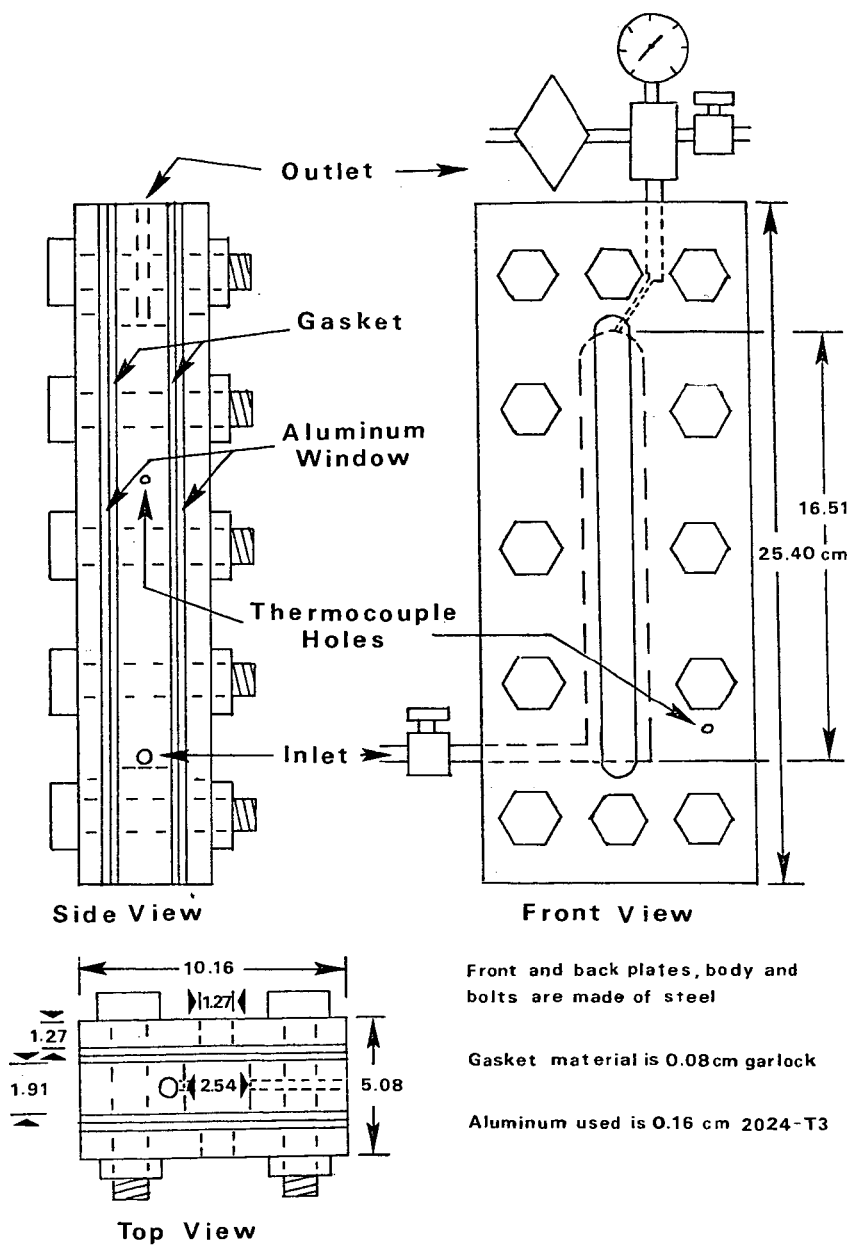
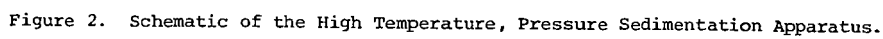


Figure 1. Schematic of the Sedimentation Cell.



A wet test meter measures the nitrogen exiting the sedimentation cell during filling. This gas flow is used to calculate the volume of the liquid entering the cell.

In addition to sedimentation, this system has the capability of filtering a sample from the autoclave for characterization of the solids. Two high temperature and pressure filter holders from Millipore Corporation are used in the filtration of the treated coal liquid. This filtration system is secondary to the experimental procedures presented in this paper.

A Diano Corporation x-ray system is employed which consists of an x-ray head and a power supply with variable voltage and amperage controls. The spread of the x-ray beam from a 0.25 mm beryllium window, covers the area of the cell and the film in the 0.46 meter distance used. A lead lined box was constructed to house the x-ray head, the settling chamber, and the film holder. The film holder, shielded by a slotted lead sheet, is movable so that eight exposures can be taken at eight time intervals on one sheet of film.

An E-C Corporation automatic densitometer, employing a constant velocity film support, is used to analyze an intact 5 x 7 sheet exposed x-ray film containing the information of one complete experiment. The densitometer is connected to a Sargent-Welch recorder which plots a graph for each exposed portion (eight in all) on the film.

Safety requires that the x-ray be shielded to protect individual workers. The unit is completely contained in a lead box. Pressure relief valves are located on the sedimentation cell and the autoclave. Care is taken in the handling of the chemicals and coal liquids used due to the fact that the materials may be carcinogenic.

PROCEDURE

The sedimentation chamber is pressurized with nitrogen and then heated to operating temperature. During this process the autoclave is charged with coal liquid and brought to operating temperature. Solvent is added unheated to the charged autoclave and mixed for a period of time. The resulting temperature after mixing of the SRC filter feed with a solvent will sometimes be lowered depending upon the amount of solvent added. Thus, sometimes the initial temperature of the SRC filter feed will be higher such that after solvent addition, the mixture will be near the desired temperature.

After the SRC filter feed has been mixed with the additive for the prescribed time and mixing speed, it is transferred to the sedimentation cell by using a nitrogen pressure difference between the cell and the autoclave.

After the pressure and temperature in both the cell and autoclave are equalized, the wide throated valves between the sedimentation cell and autoclave are opened. Tank nitrogen is opened to the autoclave at the same pressure. Then the flow into the settling chamber is controlled by the gas valve on top of the sedimentation cell thus avoiding high shear

between the autoclave and the sedimentation cell. The amount of material in the cell is calculated from the gas effluent measured with a wet test meter which is connected to the valve on top of the settling chamber. After the sedimentation cell has been filled (30 seconds), the valves are closed and the sedimentation process is monitored by x-ray photography. The time of exposure and the intensity of the x-rays is set to yield the maximum sensitivity in the important solids concentration range.

Upon completion of the sedimentation measurements, the contents of the sedimentation cell is forced back into the autoclave and parts of the system are dismantled for cleaning.

The x-ray system also has the capability of chemical additive addition in the ppm range to promote agglomeration of the particles in coal liquids. This can be accomplished by first dissolving the material in a suitable solvent and adding the solvent, or the chemical additive can be placed in a plug and blown in at the desired time with nitrogen pressure. The system also will work with gaseous additives through the replacement of the nitrogen cylinder with one containing the desired gas.

X-RAY MEASUREMENTS

After the start of settling, x-ray pictures were usually taken at intervals of 2, 4, 6, 8, 10, 20, 40 and 60 minutes. If slower settling was expected, the time intervals would be lengthened. A combination plexiglass stand and film holder positioned the x-ray film for each exposure. A lead sheet with 0.635 cm slit placed behind the aluminum window of the cell protected the remainder of the film from being exposed.

Kodak AA x-ray film is developed in Kodak x-ray developer and fixed for the prescribed period of time. The film is then washed and rinsed in Photo-flo and dried. Usually the density difference of the settling interface is visible to the eye and corresponds to the densitometer readings.

An x-ray photograph of SRC filter feed at 260°C, shown in Figure 3, depicts the interfacial settling zone as well as the compression zone at different time intervals. The compression zone could not usually be seen with the eye and densitometer readings were used to detect the top of the compression zone.

An independent experiment was conducted to prove that the visual observation of the interface in a plexiglass cell was identical to the corrected interface from the x-ray film. Neutralized acid mine sludge was used as the system. Data points plotted in Figure 4 proves that the visual and densitometer readings are in agreement.

FILM INTERPRETATION

The film was placed as near the sedimentation cell as possible, yet the results needed to be corrected for the spread of the x-rays between the cell and the film. The correction for the measured height on the film versus the actual height in the sedimentation cell is found by

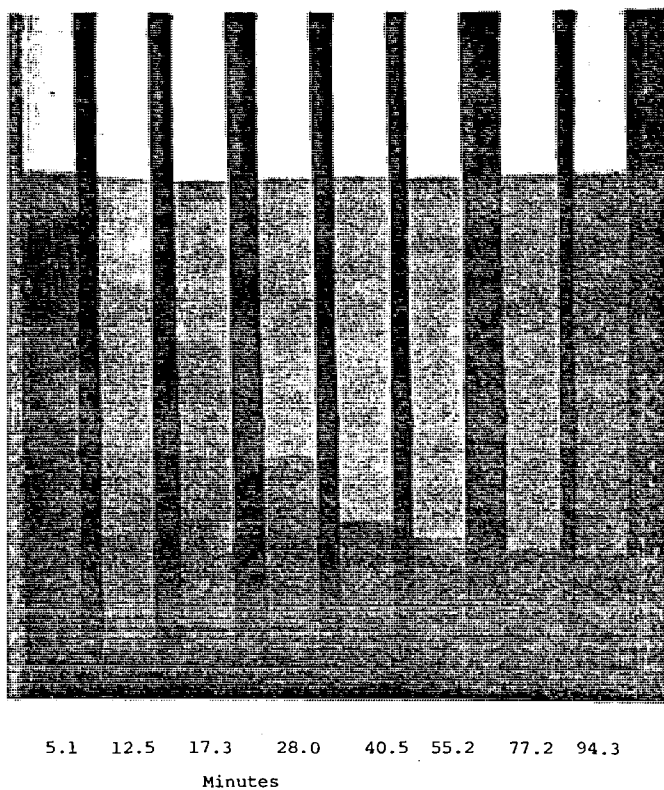


Figure 3. Photograph of X-Ray Negative of SRC Filter Feed at 260°C in the Sedimentation Cell Taken at Time Intervals Shown. Settling Interfaces and Compression Interfaces can clearly be seen.

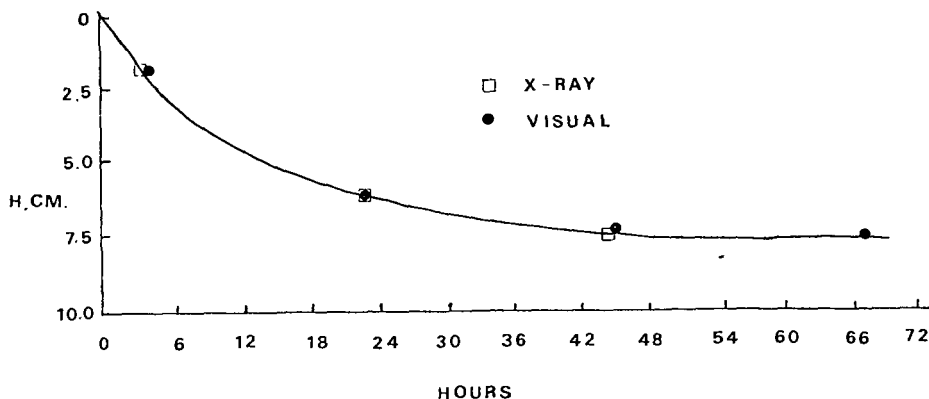


Figure 4. X-ray Versus Visual Determinations of Interface Height of Acid Mine Drainage.

geometry. An angle θ from the point source (pointed at the bottom of the cell) is identical to the angle of the x-rays through the liquid in the cell. A ratio of the height in the liquid to the height on the film can be obtained to get a correction factor of 0.83. The film height is multiplied by this factor to give the height in the cell. Nine data points were obtained for the settling zone and for the compression zone from the eight densitometer plots (the first data point being the initial height at time zero).

These corrected points were plotted to find the initial settling rate and the height of the compacted solids. Figure 5 represents an interfacial and compression curve for SRC filter feed at 260°C. Corrected height is plotted against time for the top curve (interfacial height) and the bottom curve (compression height). The height of the compression region increases with time as would be expected until the compression zone and the interfacial zone meet. The solids accumulating are loosely packed and further compression occurs after the interface meets the compression zone.

Figure 6 shows how antisolvent concentration affects the settling of solids in SRC filter feed at 260°C. This is one example of the type of data obtained from experiments where the antisolvent, mixing speed, mixing time, temperature and concentration are varied.

Note: sequential mixing, short period at high speed to distribute the solvent followed by a long period of low speed to promote agglomeration, was employed.

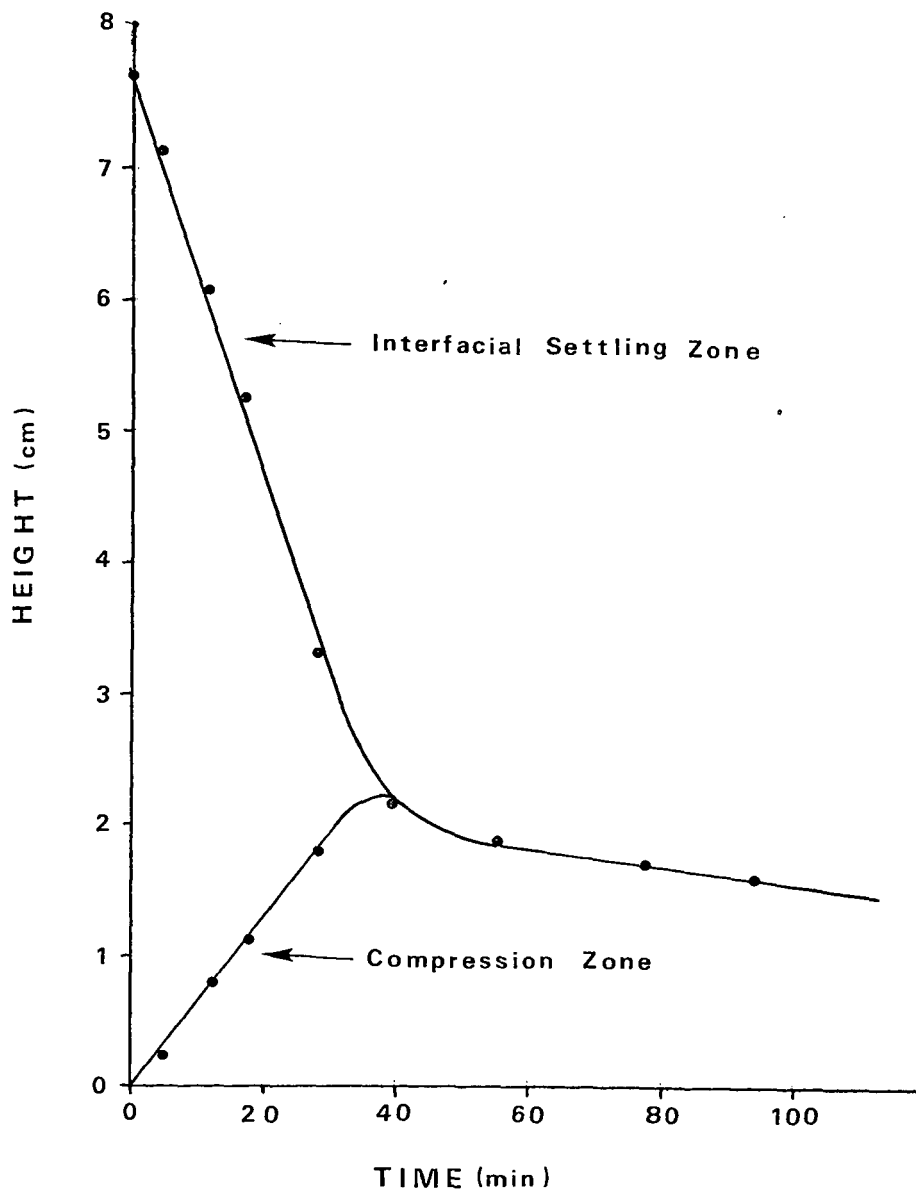


Figure 5. Corrected Settling Curve for SRC Filter Feed at 260°C.

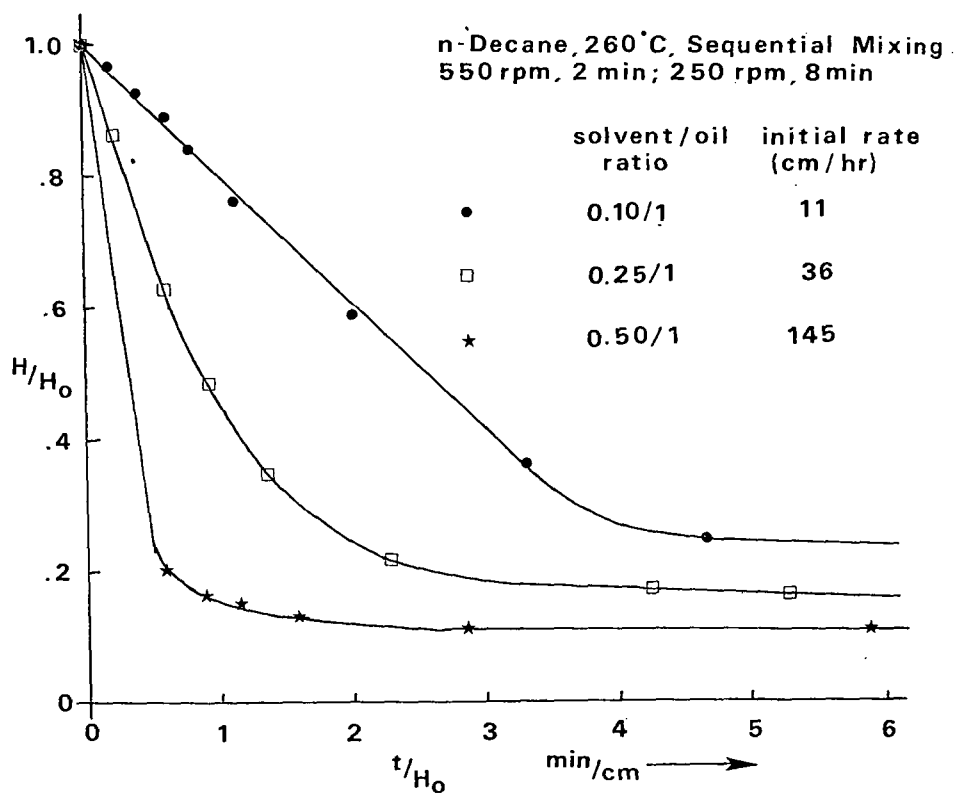


Figure 6. Influence of Solvent/Oil Ratio on Initial Settling Rate for the SRC/n-Decane System.

Since the same amount of liquid was not introduced into the cell each time, the plots of height versus time were made into dimensionless plots. All interfacial curves start at one, but have the same slope as the nondimensionless plots. The intercept of the initial slope line with the abscissa is equal to the inverse of the initial sedimentation rate.

The sequencing of this new x-ray technique is illustrated in Figure 7. From the x-ray negative (a), four densitometer plots (b) are presented to show the interface heights change as a function of time. The interface heights of both the settling and compression zones from (b) are plotted versus time to give plot (c). A dimensionless plot (d) is made from (c) to normalize the experiment. All experiments are plotted with dimensionless ordinates.

REPRODUCIBILITY

The SRC filter feed/n-decane system was chosen for the reproducibility studies. Three identical runs were made during the three month period of experimentation. The initial settling rate data using SRC filter feed from the same container of a 0.25:1 ratio with n-decane at 260°C is 36 cm/hr for the first run, 32 cm/hr for the second run and 33.8 cm/hr for the third. These slopes are within the calculated error associated with the calculations of initial settling rate (slope determination). The slope of the line is very critical and a slight deviation in drawing the line will lead to an error of 3 cm/hr out of 30 cm/hr for a shallow slope and as much as 15 cm/hr out of 150 cm/hr for a steep slope. The initial curves are very close in the first twenty minutes and are difficult to separate as seen in Figure 8. Separation occurs when the slopes are drawn to the x-axis. In spite of the graphical difficulties, the reproducibility of the n-decane experiments is excellent.

CONCLUSION

A new experimental technique has been developed to observe the initial settling rate and the height of the compression region in a high temperature, pressure sedimentation experiment by x-ray photography. Time sequenced x-ray photographs are taken which produce an observation of the position of both the settling interface and the height of the compression region. This experimental technique permits the measurement of high temperature and pressure sedimentation without direct sampling during the course of the sedimentation experiments. This offers the advantage of not disturbing the settling process and eliminates the need for time consuming chemical analyses of the mineral matter solids.

The x-ray sedimentation measurement provides both the initial settling rate and the height of the compression region. The initial settling rate provides information concerning the rate of sedimentation and the height of the compression region provides information concerning the maximum recovery of the clarified oil. This technique can be used for other settling phenomena in clear or opaque liquids which would require elevated temperature and pressure.

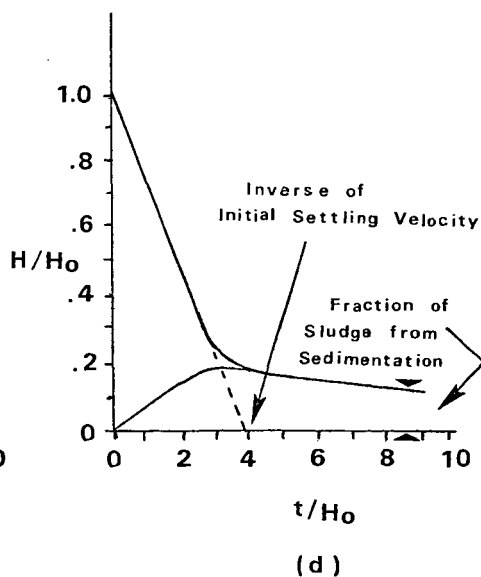
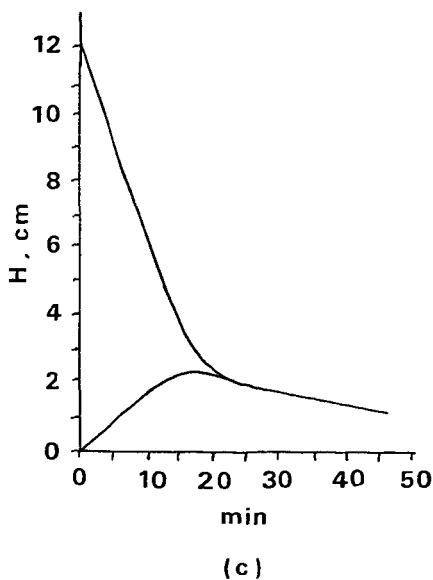
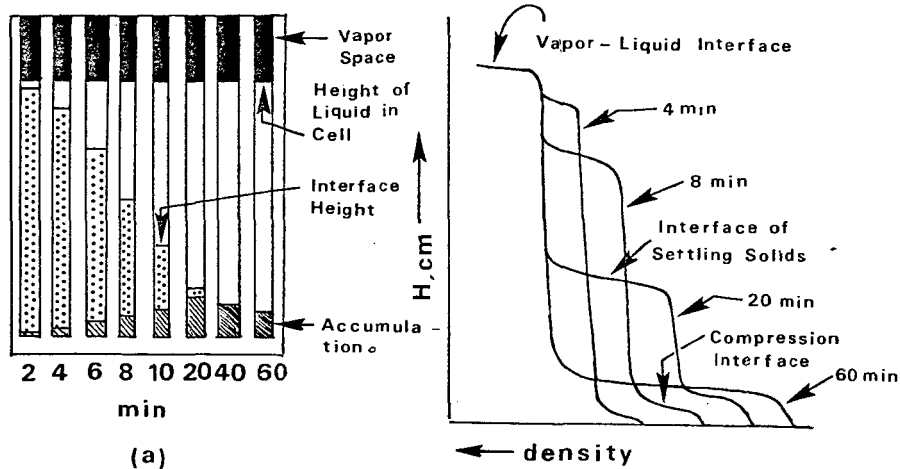


Figure 7. Interpretation of Data from X-Ray Negative to Dimensionless Plot.

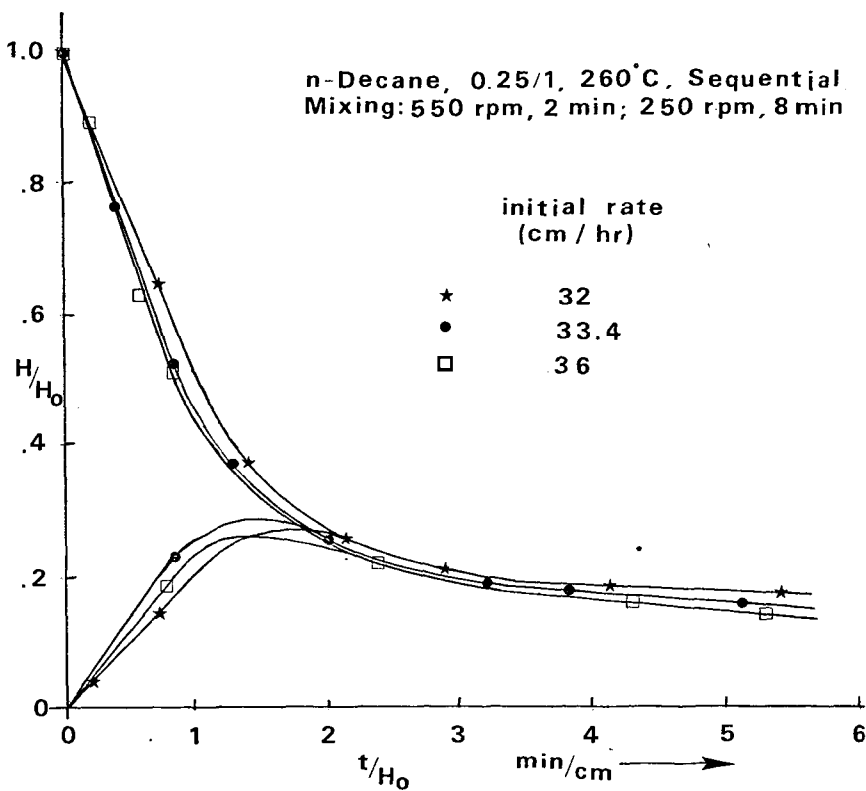


Figure 8. Reproducibility of Initial Settling Rate for SRC/n-Decane System.

ACKNOWLEDGMENTS

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LABORATORY STUDIES FOR SEPARATION OF
SOLIDS FROM SYNTHOIL GROSS PRODUCT*

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ABSTRACT

A variety of proprietary surfactants and agglomerating agents have been added to coal-liquefaction product (from the SYNTHOIL process) to determine the effectiveness of these agents in decreasing the viscosity of the product or inducing agglomeration of suspended solids in the product. More than two dozen additives were tested, but only two of the additives caused a reduction in the viscosity of the coal-liquefaction product. Two of the additives that reduced viscosity and five agglomerating agents were evaluated to determine if they could improve the settling of solids in the SYNTHOIL gross product. No improvement in solids settling was observed. In other tests, a number of organic solvents have been added to the SYNTHOIL gross product to determine their effectiveness in promoting the precipitation of suspended solids in the product. High-temperature settling of the product in the absence of a foreign solvent does not appear to be a promising mechanism for solids removal from this product. However, the promoter-solvent de-ashing scheme has been demonstrated to be a potentially attractive solids-liquid separation method, and kerosene had been found to be an effective promoter solvent for the SYNTHOIL gross product.

INTRODUCTION

A difficult technical problem encountered in the development of any coal liquefaction process is the removal of solids (carbonaceous solids and ash) from the product stream. This step is troublesome because coal-liquids are viscous and contain high concentrations of suspended solid residues; a substantial fraction are in the micrometer size range. This problem is particularly severe for those processes (such as the SYNTHOIL process under development by Pittsburgh Energy Research Center) aimed at producing boiler fuel with minimum hydrogenation, because with less hydrogenation, a more viscous product is produced. To meet the sulfur oxide and particulate emission standards for direct combustion of coal oil and to avoid fouling and poisoning of catalysts in further processing of coal oil, a substantial fraction of the solids in the oil must be removed.

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A complete solids-liquid separation scheme generally involves four basic steps. They are pretreatment, solids concentration, solids separation, and post-treatment. To optimize a separation, all four steps must be carefully considered. Although it has been recognized that successful pretreatment or solids concentration can greatly simplify the entire separation operation, this type of approach has not been fully applied to coal-liquefaction studies. Most efforts on solid-liquid separation have addressed the solids-separation step only. A recent paper by Batchelor¹ indicated that the cost increment for removal of solid residues from coal-liquids was quite substantial, and research and development work in this area was necessary for successful commercialization of any liquefaction process.

In this paper, we present results from our laboratory studies for separation of solids from SYNTHOIL coal-liquefaction product. The studies consisted of two parts. In the first part, the use of commercially available additives (chemical pretreatment) to facilitate the removal of solid residues from the SYNTHOIL product stream was attempted. Our effort was aimed at either reducing the viscosity of the SYNTHOIL gross product or inducing settling of suspended solids in the gross product, by the addition of a small amount of chemicals. In the second part of our studies, the high-temperature settling and the promoter-solvent de-ashing schemes were explored for their effectiveness to the SYNTHOIL gross product. The organic solvents examined in the promoter-solvent de-ashing experiments ranged from solvents which dissolve only the heavy-oil fractions of the coal-liquids to solvents which dissolve all organic materials present.

EXPERIMENTAL

Materials

The SYNTHOIL gross product (uncentrifuged product), made from West Virginia coal (Pittsburgh seam of Ireland Mine), was supplied by the Pittsburgh Energy Research Center (PERC). This product oil was produced in a nominal 1/8 in. x 1/8 in. Pyrex glass cylinders; working conditions were 4,000 psig and 450°C; 35 percent solid slurry was fed on lined-out, coal-derived oil at 25 lb per hour. Table 1 gives the results of chemical property analyses of a sample of this product. Figure 1 shows the temperature-viscosity relationship, determined by using a Brookfield viscometer described below.

Chemical additives were provided by DuPont Chemical Company, Nalco Chemical Company, Emery Industrial, Inc., and the Tetrolite Division of the Petrolite Corporation. Three broad classifications of additives were studied; anionic, cationic, and non-ionic which had either amide or sulfonate functional groups.

All hydrocarbon liquids, except kerosene and fuel oil, used in the promoter-solvent de-ashing tests were obtained from Fisher Scientific Company, and are at least technical grade. The kerosene and the fuel oil were purchased from a local vendor.

Table 1. Chemical Property Analyses
of SYNTHOIL Gross Product.

Product	wt %
Benzene-Solubles	86.7
Heavy Oil	59.9
Asphaltenes	26.8
Benzene-Insolubles	13.3
Ash	4.9
Organics	8.4
Ultimate Analysis	
C	85.0
H	7.5
N	1.3
S	1.1

Table 2. Properties of DuPont Surfactants.

	Petrowet R	Alkanol WXN
Chemical type	Anionic	Anionic
Active ingredient	Sodium-dodecyl sulfonate	Sodium-dodecyl benzene sulfonate
Concentration of active ingredient	22%	30%
pH, 1% of sorbent in water	4.0 to 5.5	7.5 to 9.0
Flash point	91°C	100°C
Density, lb/gal	9.0	8.6
Solubility in H ₂ O	Miscible	Miscible
Stability		
Acid	Stable	Stable
Alkali	Stable	Stable

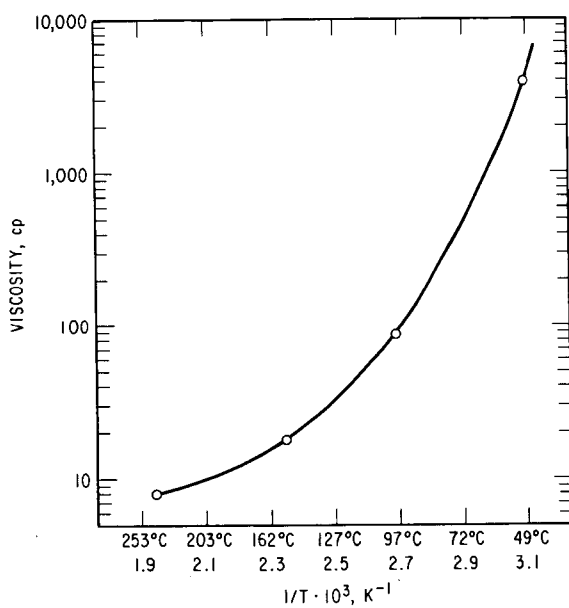


Figure 1. Viscosity-Temperature Behavior of SYNTHOIL Gross Products.

Procedures

Viscosity Reduction. A Brookfield Model LVT Synchro-lectric viscometer was used for the viscosity measurements of the SYNTHOIL products. This unit, along with a Brookfield Thermosel System to heat the sample, permitted us to obtain viscosities of liquid samples between 5 and 10,000 cp with a precision of 1%, at temperatures between ambient temperature and 260°C. Measurement of the temperature inside the liquid-sample container of the Thermosel was accomplished with a calibrated copper-constantan thermocouple; agreement with the set temperature on the controller was within 1%. To minimize the oxidation effect of the oil sample, the viscosity-measuring unit was confined in a Plexiglas enclosure that was continuously purged with nitrogen.

Additive-Induced Settling. In the settling tests, the effectiveness of each additive was judged by its effect on the extent of settling (for a chosen time) of suspended solids when the additive was added to SYNTHOIL gross product. Copper tubes, 3/4-in. OD (about 2 cm² in inner cross-sectional area) and 40 cm long, were used as settling columns. A measured amount of each chemical was added to a measured amount of SYNTHOIL gross product to make an approximate 65-ml mixture of the desired composition. The mixture was thoroughly stirred at 80°C for 10 min, and was then immediately transferred to the copper tube. The top of the tube was closed with a copper Gyrolok cap. The tube was then placed in a silicone oil bath for a prescribed time interval and the temperature was regulated with a Bayley Model 124 Precision temperature controller to within ±2°C of the set temperature (150-350°C). After careful removal from the oil bath, the tube was chilled in ice water and subsequently dipped in liquid nitrogen to quickly solidify the liquid sample; it took about 10 min to complete these two steps. The frozen sample was then divided into six fractions by cutting the copper tube with a tubing cutter into six 5-cm-long sections. Each fraction was analyzed for ash and sulfur contents by a standard ASTM method (D271) and a Leco technique, respectively.

Promoter-Solvent De-ashing. The same procedure described above in the additive-induced settling was used also in de-ashing tests to judge the effectiveness of each solvent. However, the mixing temperature was maintained at 60°C instead of 80°C.

RESULTS AND DISCUSSION

Viscosity Reduction

The following commercially available chemicals were tested for their abilities to reduce the viscosity of SYNTHOIL products: DuPont's Alkanol BG, Alkanol WXN, Alkanol 189-S, Duponol SP, Duponol WAQE, Petrowet R, Product BCO and Zonyl A, Nalco's 81C09, NALCOAL 8863 and NALCOLYTE 8861, Ivory soap, Emery's Emerest 2400, 2410 and Emsorb 2500, 2503, 2505, 2515, 6903, 6915, and Tretolite's TFL-313, TFL-330, TFL-366, 771-119, 772-238 and 771-139.

Of these chemicals, only two DuPont surfactants had a significant effect (>10% viscosity reduction) on the viscosity of the SYNTHOIL products;

they have been investigated in detail. The effective DuPont surfactants are Petrowet R and Alkanol WXN. Petrowet R is a solution of sodium dodecylsulfonate in water and isopropyl alcohol, and Alkanol WXN is a solution of sodium dedecyl benzene sulfonate in water. Their properties are listed in Table 2.

Viscosity measurements were made on SYNTHOIL gross product, to which had been added various amounts of Petrowet R or Alkanol WXN, as the samples were heated from 82°C to 120 or 140°C and again at the same temperature as the samples were cooled. The complete results are shown in Table 3. The estimated precision of the percent viscosity reduction values is about 2%.

As can be seen from the results for 0.91 wt % Petrowet R and 1.29 wt % Alkanol WXN in Table 3, when the sample was heated to 140°C, the percentage reduction in viscosity due to the additive was not reversible upon decreasing the temperature. The viscosities obtained at the lower temperature upon decreasing the temperature were equivalent to those obtained in the absence of additive. Reversibility was only partial when the temperature maximum had been 120°C.

At 82°C, the addition of 1 wt % "Petrowet" R reduced the viscosities of the gross product by 11%; the viscosity of the gross product was reduced by 14% by the addition of about the same amount of "Alkanol" WXN. However, the magnitude of the reduction in viscosity decreased as the temperature was increased, and there was essentially no reduction in viscosity at 140°C due to additive. Furthermore, if 1 wt % additive were used, the cost contribution of these two additives to the production cost of one barrel of oil would be approximately \$2.40, which is high from a practical viewpoint.

Additive-Induced Settling

Researchers at Oak Ridge National Laboratory, using small sedimentation tubes, have observed²⁻⁴ that certain liquid additives in low concentration (1,000 ppm) significantly increased the settling rate of suspended solids in the SRL* (Solvent Refined Liquid) of the SRC (Solvent Refined Coal) process. The most promising additive (Tretolite 771-119) appeared to provide at least a factor of five improvements in comparison to the settling rate of untreated SRC oil and to be valid over a wide (210 to 350°C) temperature range. Since the small amount of additives had a practically negligible effect on the viscosity of the SRC unfiltered oil, the improvement in settling is believed to be due to the agglomeration of solid residues, or the coprecipitation of asphaltene and ash. It was believed that if similar results could also be obtained for the SYNTHOIL gross product, the solids agglomeration induced by additives would greatly simplify subsequent separation steps.

*The solvent refined liquid is the unfiltered combination of dissolved coal and solvent.

Table 3. Effect of Additives on Viscosity of SYNTHOIL Gross Product.

For each concentration, viscosity measurements were taken with temperature increasing to the temperature maximum and then with temperature decreasing.

Additive Weight (wt %)	Viscosity ^a (cp)						
	82°C	100°C	120°C	140°C	120°C	100°C	82°C
0	241.	82.8	37.0	21.3	37.2	85.2	275.
0	242.	83.0	37.4		37.4	83.8	247.
<u>Petrowet R</u>							
0.06	240. (0.8)	82.7 (0.4)	36.8 (1.6)		36.8 (1.6)	83.0 (1.0)	244. (1.2)
0.16	232. (4.1)	80.2 (3.4)	36.2 (3.2)		36.2 (3.2)	81.5 (2.7)	234. (5.3)
0.45	221. (8.7)	76.5 (7.8)	35.7 (4.5)		35.7 (4.5)	80.5 (3.9)	240. (2.8)
0.91	218. (9.5)	75.0 (9.4)	35.4 (4.3)	21.2 (0.5)	37.2 (0.0)	85.4 (0.0)	276. (0.0)
1.47	216. (10.8)	75.0 (9.6)	35.5 (5.1)		35.5 (5.1)	80.5 (3.9)	233. (5.7)
<u>Alkanol WXN</u>							
0.39	228. (5.8)	79.0 (4.8)	36.2 (3.2)		36.2 (3.2)	80.4 (4.1)	240. (2.8)
0.63	211. (12.8)	74.5 (10.2)	35.0 (6.4)		35.0 (6.4)	76.4 (8.8)	228. (7.7)
1.13	209. (13.6)	73.2 (11.8)	34.8 (7.0)		34.8 (7.0)	76.6 (8.6)	228. (7.7)
1.29	208. (13.7)	72.5 (12.4)	34.7 (6.2)	21.0 (1.4)	37.0 (0.5)	84.5 (0.8)	274. (0.4)

^aPercentage reductions in viscosity

$(100 \times \frac{\text{Viscosity of Gross Product} - \text{Viscosity of Gross Product with Additive}}{\text{Viscosity of Gross Product}})$
are in parentheses.

Seven chemicals have been evaluated using the settling test. They are: Nalco's 81C09, NALCOAL 8863 and NALCOLYTE 8861, DuPont's Petrowet R, and Alkanol WXN, and Tretolite's 771-119 and 772-238. Experiments with the first five additives were conducted at 200°C and with the last two additives at 250°C; settling time was 4 hr. Comparison of the results with the results for blank tests showed no significant additional settling of solid residues. The disparity of the effect of Tretolite's 771-119 on SYNTHOIL gross product with the results obtained for SRL at ORNL is not surprising because SRL differs considerably from the SYNTHOIL gross product.*

High-Temperature Settling

Scouting studies by research workers at Oak Ridge National Laboratory (ORNL)⁵ also showed that high-temperature settling is a promising mechanism for solids separation from SRC (Solvent Refined Coal) unfilter oil. They also noticed that during the course of settling at elevated temperatures, suspended solid residues agglomerated, probably due to softening of high-molecular-weight hydrocarbons coated on the surface of the solid residues; consequently, the solids stuck together upon collision.

Table 4 gives representative settling results for SYNTHOIL gross product at 200 and 250°C. Unlike the results observed by Oak Ridge workers for SRC unfiltered oil, no great settling of the SYNTHOIL gross product occurred in 4 hr. Even after settling for the impractical time interval of 24 hr, the top fraction was not clear. Also, settling was only slightly improved when the settling temperature was increased from 200°C to 250°C.

Using the Stoke's equation and the viscosity results from Fig. 1, we calculated the settling velocities of a 6- μ m spherical solid particle at 200°C and 250°C; they are 0.7 cm/hr and 1 cm/hr, respectively.⁶ Because it fails to take the shape effect of suspended particles and the interactions between individual particles into account, the Stoke's equation does not provide accurate predictions of the settling velocities for a complex system of high solid concentration and wide particle-size range. Nevertheless, this equation can be used to calculate an upper limit for settling velocity. Since about 30 wt % of solid particles in the SYNTHOIL gross product are in the size range under 6 μ m, the smallness of the calculated value of settling velocities, in conjunction with the preceding experimental results, suggest that in the absence of a second solvent, high-temperature settling is unlikely to be a practical separation scheme for the SYNTHOIL process stream.

High-Temperature Settling with Solvent

Promoter-solvent de-ashing has been demonstrated to be a promising scheme of removing suspended solid residues from the product stream for a variety of coal-liquefaction processes;⁷⁻¹⁰ however, the mechanism behind

*In their recent progress report (ORNL-5208), however, ORNL researchers indicated that the significant improvement (at least a factor of 5) observed with small sedimentation tubes could not be found with their bench-scale settler.

Table 4. Analyses of Settling Fractions of SYNTHOIL Gross Product (4.9 wt % Ash, 1.1 wt % S).

Settling Temperature (°C)	Settling Time (hr)	Fraction ^a No.	Ash (wt %)	Sulfur (wt %) ^b
200	4	1	4.1	1.1
		2	4.1	1.0
		3	4.1	1.0
		4	4.2	1.1
		5	4.2	1.3
		6	5.4	1.3
200	24	1	0.54	0.67
		2	1.6	0.67
		3	3.0	0.87
		4	6.9	1.2
		5	7.9	1.3
		6	9.6	1.5
250	4	1	4.0	
		2	4.0	
		3	4.0	
		4	4.0	
		5	4.0	
		6	8.1	

^aEach fraction is 5 cm long; fraction numbers are in order from the top to the bottom of a sample.

^bThe estimated precisions are 5% for ash and 10% for sulfur.

its success is still not fully understood. It has been suggested that the presence of a second liquid phase causes the heavier asphaltic materials to precipitate by lowering their solubility limit to the heavy-oil phase. It is also very possible that some of the solid particles would act as sites for the initiation of precipitation and that, as the precipitation process continues, some of the solid particles would stick together, forming large aggregates.

The selection of effective promoter solvents for different liquefaction products is, nevertheless, largely an art. Some controversy exists between investigators on the effectiveness of a promoter liquid. For instance, Gorin and coworkers⁸ stated that, on a weight basis, n-paraffins from n-butane to n-decane, cyclohexane, and decalin were approximately equally effective in de-asphalting and reducing the ash content of a CSF (Consol Synthetic Fuel) product stream. However, Sze and Snell¹⁰ concluded that hexane, being a paraffinic liquid, is not an effective promoter solvent for a Lummus liquefaction product.

In our study, the following organic liquids were tested: n-hexane, n-octane, No. 2 fuel oil, kerosene, toluene, tetralin, and tetrahydrofuran. The n-hexane is believed to dissolve only the heavy-oil fractions of the coal-liquefaction product; the tetrahydrofuran is able to dissolve nearly all of the organics. The rest of the solvents have intermediate solvent powers. N-octane has a solvent power close to that of n-hexane; the solvent powers of tetralin and toluene are close to that for tetrahydrofuran. Because of the complex nature of the coal-liquefaction product, the true solvent power of each solvent to the product could not be accurately estimated.

Representative results for settling runs with toluene, n-octane, and kerosene are tabulated in Table 5. Tetralin and tetrahydrofuran gave results similar to those for the toluene, and the results for n-hexane and No. 2 fuel oil were slightly inferior to those for the n-octane. These results clearly support Sze and Snell's finding^{9,10} that, of the solvents we have tested, kerosene is the most effective and promising promoter solvent for the SYNTHOIL gross product. The settling efficiency of solid particles appears to increase as the concentration of the promoter solvent increases. The results for settling runs using 30 wt % kerosene are especially good, resulting in three top fractions of almost ash-free oil. When the settling temperature was increased from 200°C to 250°C, the settling time required to obtain three clear oil fractions was reduced from 6 hr to 4 hr, indicating that temperature also plays an important role in the settling process.

In an attempt to partially verify the speculation that the function of the added promoter solvent is to induce the precipitation of heavy asphaltenes, we measured the viscosity of each fraction from the 200°C settling run with 30 wt % kerosene. The results are presented in Table 6. Also shown in the table are viscosities of the SYNTHOIL gross product-kerosene mixture at several temperatures. The viscosity results for the bottom two fractions (5 and 6) are much greater than those for other four fractions, and a clear viscosity gradient exists from the top to the bottom. It is well known that the viscosity of the coal liquefaction product increases greatly with increasing asphaltene content.¹¹ The viscosity results thus support the suggestion that most of the heavy asphaltenes precipitated and settled in the bottom fractions during the course of settling.

One point regarding the promoter-solvent de-ashing method that should be emphasized is that although the major advantage of this method is elimination of the troublesome rotational equipment associated with filters and centrifuges, its economic justification is highly dependent on recovery and recycling of the promoter solvent. To facilitate recovery, it is desirable that a boiling point gap exists between the promoter solvent and the front end of the coal-liquefaction product treated. It has been suggested⁹ that the low-boiling fractions of the coal-derived complex first be driven off to provide the boiling point gap. However, for the SYNTHOIL process, the primary goal is to produce nondistillable boiler fuels, and the boiling-point gap desired is naturally built in.¹² Consequently, the promoter-solvent de-ashing scheme should be particularly useful in the SYNTHOIL process.

Table 5. Analyses of Settling Fractions of SYNTHOIL Cross-Solvent Mixtures.

Solvent	Settling Temperature (°C)	Settling Time (hr)	Fraction No.	Ash (wt %)	Sulfur (wt %)
20 wt % toluene	200	4	1	2.1	0.91
			2	2.5	0.94
			3	2.6	0.96
			4	2.7	0.95
			5	2.5	0.98
			6	4.6	1.32
25 wt % n-octane	200	4	1	1.5	0.76
			2	2.1	0.70
			3	2.5	0.64
			4	2.7	0.78
			5	2.8	0.85
			6	7.8	1.37
25 wt % kerosene	200	3	1	0.91	0.44
			2	1.0	0.56
			3	0.8	0.55
			4	1.7	0.67
			5	5.5	1.1
			6	8.7	1.4
30 wt % kerosene	200	6	1	0.03	
			2	0.02	
			3	0.03	
			4	1.5	
			5	6.7	
			6	11.8	
30 wt % kerosene	250	4	1	0.07	
			2	0.06	
			3	0.05	
			4	1.51	
			5	6.9	
			6	11.0	

Table 6. Viscosities of 200°C Settling Fractions of SYNTHOIL Gross Product-30 wt % Kerosene Mixture.

T (°C)	SYNTHOIL-Kerosene Mixture	Fraction No.					
		1	2	3	4	5	6
50	72.4	18.8	30.6	40.8	41.5	405	>10,000
100	11.5	9.0	10.1	9.8	11.2	42	372
150	7.5	6.7	6.8	6.2	6.4	18	127
200	5.0	3.8	3.6	4.6	4.2	12.6	47.9

CONCLUSIONS

Tests of more than two dozen commercially available additives indicate that the use of additives to reduce the viscosity of coal-liquefaction product streams is not productive. The greatest reduction in viscosity observed for SYNTHOIL products is 14% at low temperature (82°C); further decreases in viscosity become smaller as the temperature increases. Such relatively small reductions in viscosity could be realized by a small increase in temperature in the absence of an additive. Furthermore, cost figures do not support the use of additives as a potential pretreatment step to reduce the viscosity of coal-liquefaction product streams.

Although additive-settling tests did not yield positive results for the SYNTHOIL gross product, chemical pretreatment has been widely applied and desirable agglomeration has been experienced in the waste water treatment area. This pretreatment step is potentially attractive and warrants more investigation.

High-temperature settling with no second solvent added is unlikely to be a practical solids-liquid separation scheme for the SYNTHOIL process stream.

The attractive promoter-solvent de-ashing method for removing solid residues from product stream has been demonstrated to be applicable to the SYNTHOIL gross product. Selection of suitable promoter solvents is the key to the success of this method, and we have found that kerosene is an effective promoter solvent for the SYNTHOIL gross product.

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PHOTOCHEMICAL H ATOMS AS A STRUCTURAL PROBE
OF THE SURFACE OF COAL¹

by

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ABSTRACT

Hydrogen atoms, produced by the mercury photosensitization of H₂, were made to interact with coal dust, -53 to +38 microns, at 200°C in a flow reactor. Illinois No. 6, Pittsburgh Seam, and Utah-Emery coals produced a large number of products in the C₂ to C₈ range. Wyoming-Wyodak coal was considerably less reactive. The kinetic, quantitative, and structural implications of these results are discussed. Experimentation with different reactor conditions continues.

INTRODUCTION

Considerable interest in the interaction of hydrogen atoms with coal surfaces has been evident for over twenty-five years,³ resulting in a review of the literature⁴ in 1965 and recent research by N. Berkowitz, et al.⁵⁻⁶ Despite this intense interest the data are conflicting, and range all the way from reports of no reaction at ambient temperature to complete gasification. Some of these discrepancies arise from the discharge technique used to generate the H atoms; coal dust probably found its way into the discharge itself in some instances. Photochemical production of H atoms was mentioned and dismissed as being too inefficient.⁴ Because of the experimental discrepancies and their probable cause, the system H · atoms + coal was reinvestigated with photochemically generated H atoms.

EXPERIMENTAL

In work reported elsewhere in this symposium it was found that cryo-crushing was the grinding method of choice if the surface of the coal was to represent bulk coal more accurately. The grinding techniques are reported elsewhere⁷ and will not be described here. The bituminous coals

¹Based in part on data to be submitted by Muthu Sp. Sundaram as a Ph.D. Dissertation.

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were dried at 200°C in an oven through which N₂ gas was passed continuously. The sub-bituminous Wyoming-Wyodak coal was dried in a vacuum oven at 100°C. Illinois No. 6, Pittsburgh Seam, Utah-Emery, and Wyodak coal samples were then cryocrushed, sieved, and stored in a nitrogen environment. Only the -53/+38 micron fractions were used in these studies.

Fifteen grams of coal were mixed with an equal weight of ground glass, +50 micron sizes, and placed on a frit, F₁, Figure 1, for dispersal in the quartz reactor. The mercury saturator was heated to near 100°C and ambient condenser water used to produce saturation. The reactor walls were heated by passing current through the nichrome heaters. The six, meter-long, germicidal lamps, 36 watts each, were cooled with rapidly flowing, filtered air and turned on. Next, a stream of H₂ sufficient to disperse the coal dust (about 300 liters/min) was initiated. Traps T₁ and T₂, packed with 1/4" glass beads, were precooled in liquid nitrogen for ninety minutes before the experiment and were by-passed initially. When the temperature in the quartz reactor reached 200°C, the liquid-N₂-cooled traps were opened and the gas by-pass closed. Throughout this period and the remainder of the experiment, the finer coal dust, which tended to accumulate on the Millipore filter, F₄ on Figure 1, was recycled using a mechanical vibrator. At the end of an hour, during which the temperature sometimes dropped as low as 185°C, the flow was discontinued and the traps were isolated for analyses.

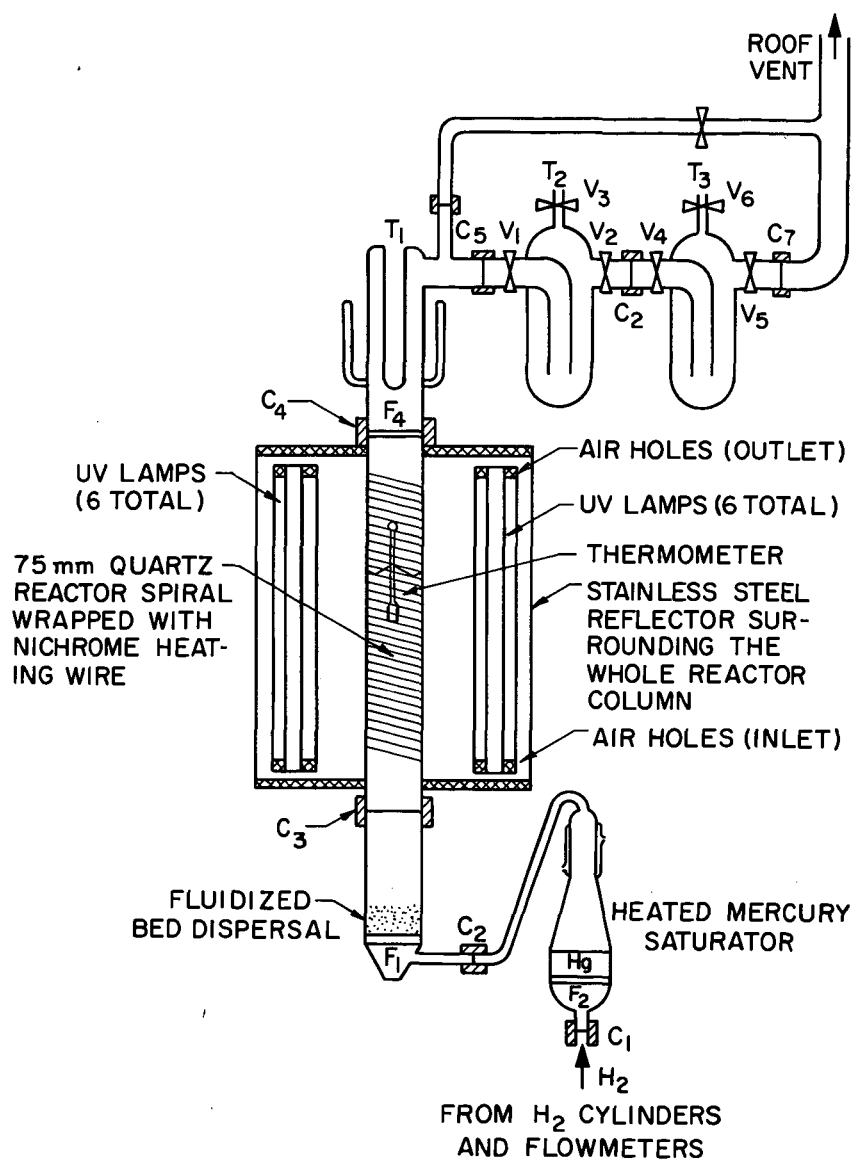
In the actinometry experiments, the identical procedure was followed except that the coal was omitted and the carrier gas contained 2% ethylene.

The traps were disconnected from the apparatus and the excess H₂ was pumped away at liquid nitrogen temperature. The residual gases, after the traps were warmed to ambient temperature for several hours, were sampled with a 25-cc sample loop and injected on to a gas chromatographic column at 60°C, 1/8" x 10', packed with n-C₁₈/Porasil C, in a Perkin-Elmer Model 990 gas chromatograph equipped with a thermal conductivity detector using 8% H₂ in He carrier gas. The resultant gas chromatograms are reproduced in Figures 2 through 5, inclusive.

RESULTS AND DISCUSSION

Because the vapor pressure of Hg was high, probably near a millitorr, most of the 2537A resonance radiation was absorbed within 0.2 cm of the quartz wall. However, the resultant excited ³P₁ Hg atoms, $\tau_0 \approx 10^{-7}$ sec, were essentially completely quenched by the atmosphere of H₂ and thus generated two H atoms per photon in this 240 cm³ zone. The extent to which the rapidly moving H atoms attained a uniform concentration throughout the vessel is not known, nor is the rate at which they were removed at the quartz reactor surface by recombination. When 2% ethylene was added to the flow stream in the absence of coal and the resultant butane, ethane, ethylene mixture analyzed, a rate of H atom formation of 2.90×10^{18} atoms/sec in the reactor was indicated. If these were uniformly distributed, 5.4×10^{14} atoms/cc/sec was the stationary state rate of hydrogen atom production and an overall steady state concentration of about 2×10^{13} H atoms/cm³ can be calculated, which compares well with those generated by discharge techniques.

Although no coal dust deposited on the walls of the quartz reactor, it did collect on the pyrex thermometer, the Millipore filter paper, F₄, and in the lower un-irradiated zone. This deposition precluded a quantitative



THE PHOTOREACTOR

Figure 1

GAS CHROMATOGRAM OF H ATOM CRACKING
PRODUCTS OF ILLINOIS NO. 6 COAL

AT 185 - 200°C

n-OCT/PORACIL C
1/8" X 10' COLUMN;
60°C; 8% H₂ IN
He CARRIER GAS;
25cc INJECTION LOOP

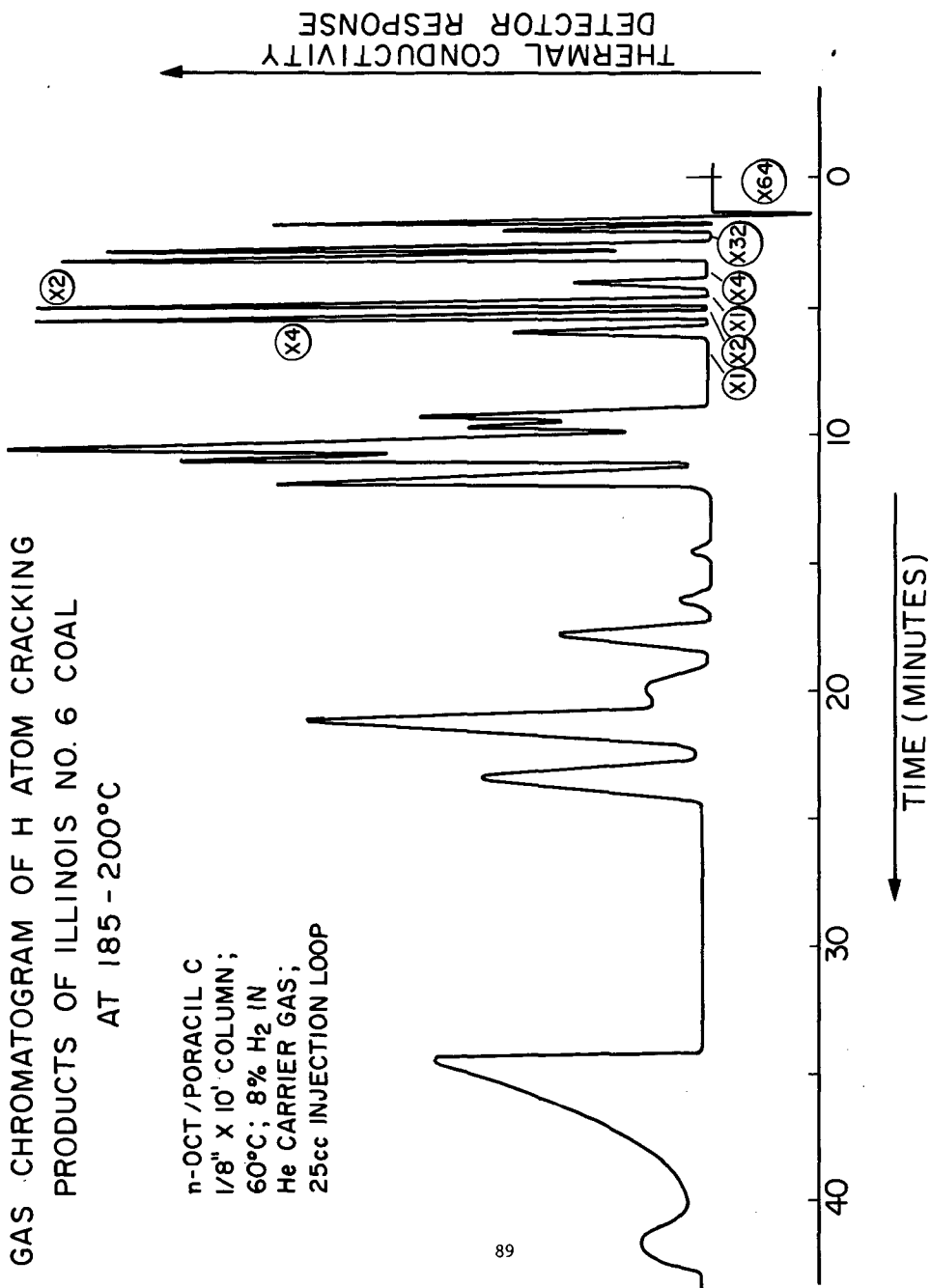


Figure 2

GAS CHROMATOGRAM OF H ATOM CRACKING PRODUCTS OF PITTSBURGH HI-SEAM

COAL AT 185-200°C

π -OCT/PORACIL C
1/8" X 10' COLUMN;
60°C; 8% H₂ IN
He CARRIER GAS;
25cc INJECTION LOOP

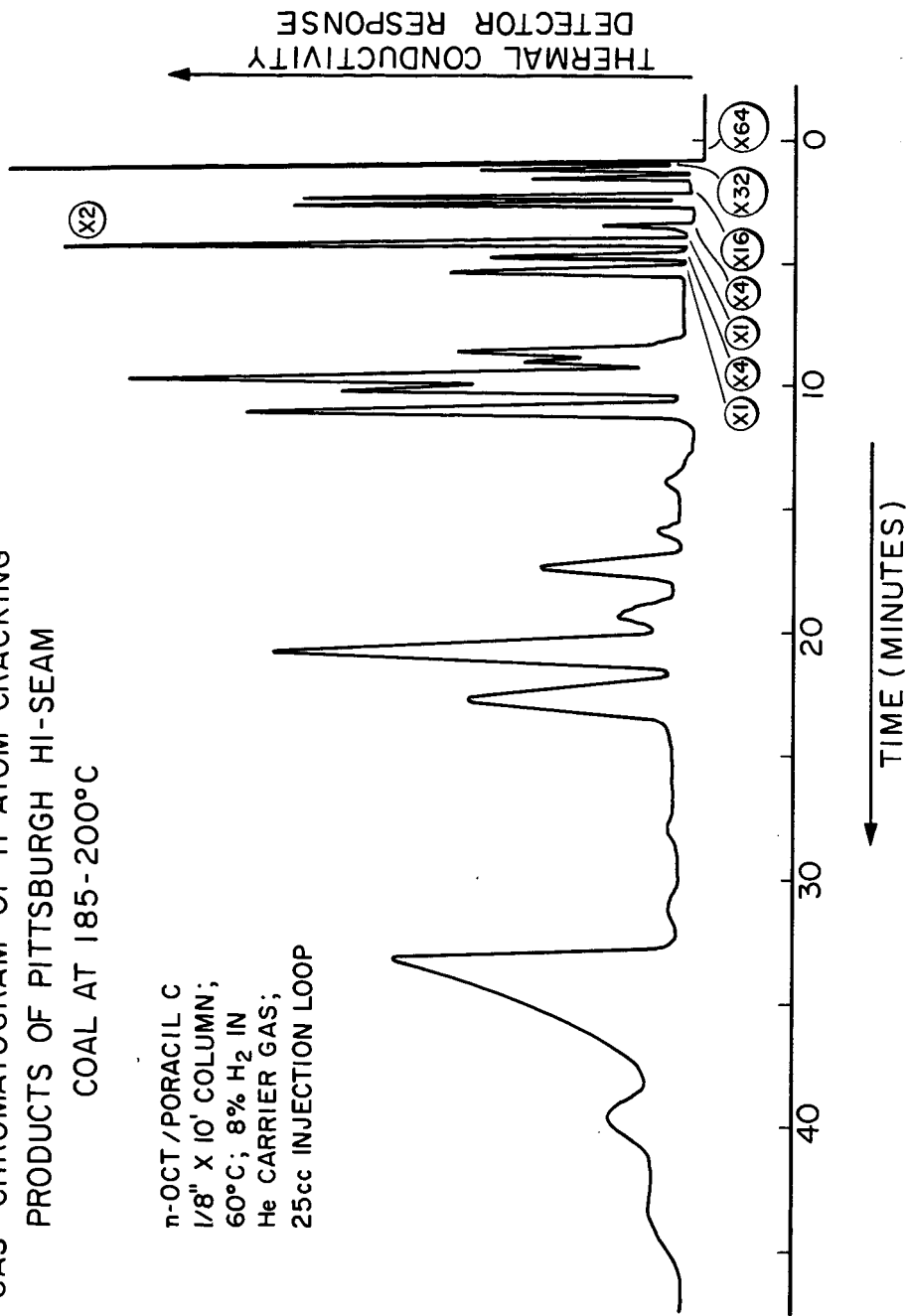


Figure 3

GAS CHROMATOGRAM OF H ATOM CRACKING PRODUCTS OF EMERY-UTAH COAL

AT 185 - 200°C

n-OCT/PORACIL C
1/8" X 10' COLUMN;
60°C; 8% H₂ IN
He CARRIER GAS;
25cc INJECTION LOOP

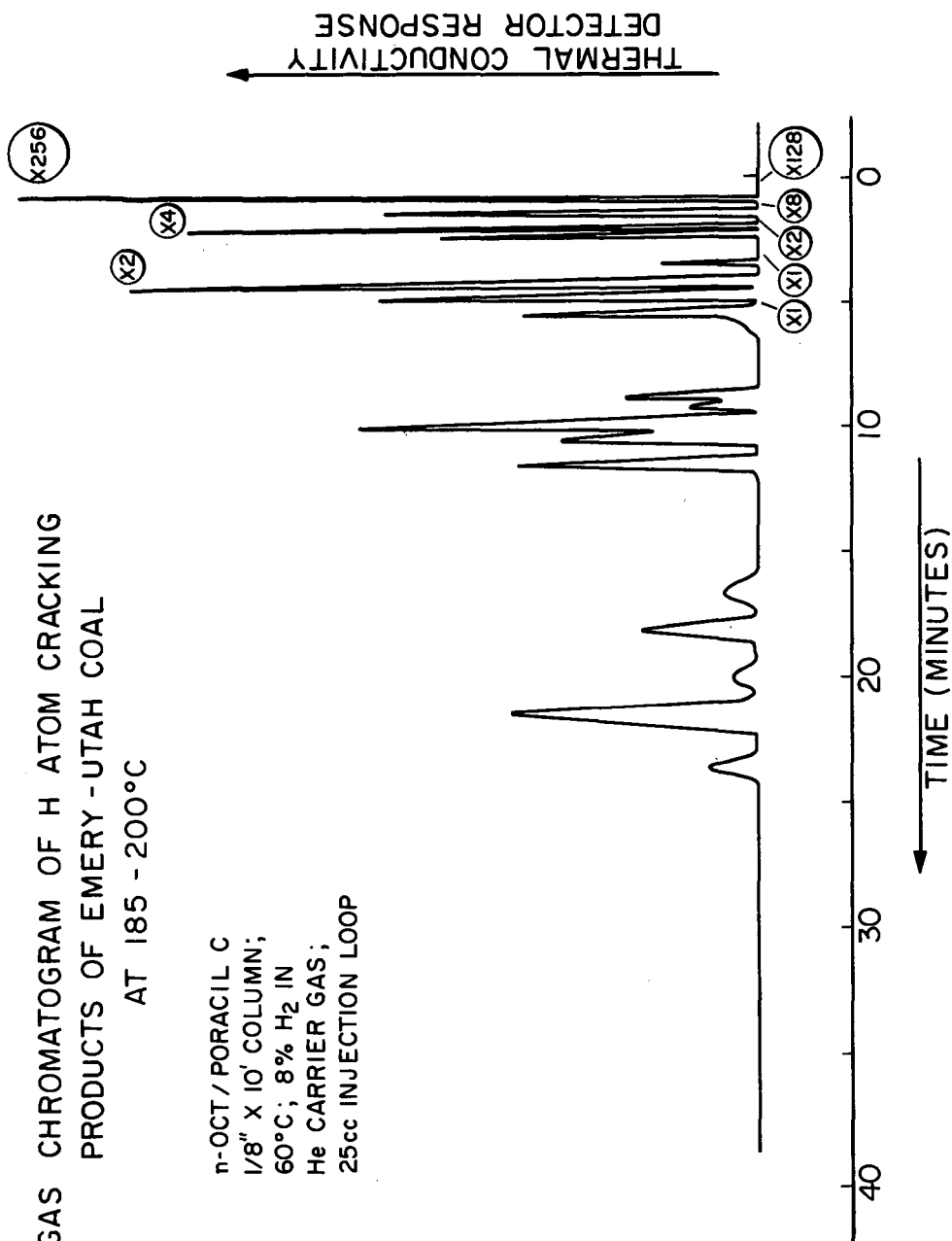


Figure 4

GAS CHROMATOGRAM OF H ATOM CRACKING
PRODUCTS OF WYOMING-WYODAK COAL
AT 185 - 200°C

n-OCT/PORACIL C
1/8" X 10' COLUMN;
60°C; 8% H₂ IN
He CARRIER GAS;
25cc INJECTION LOOP

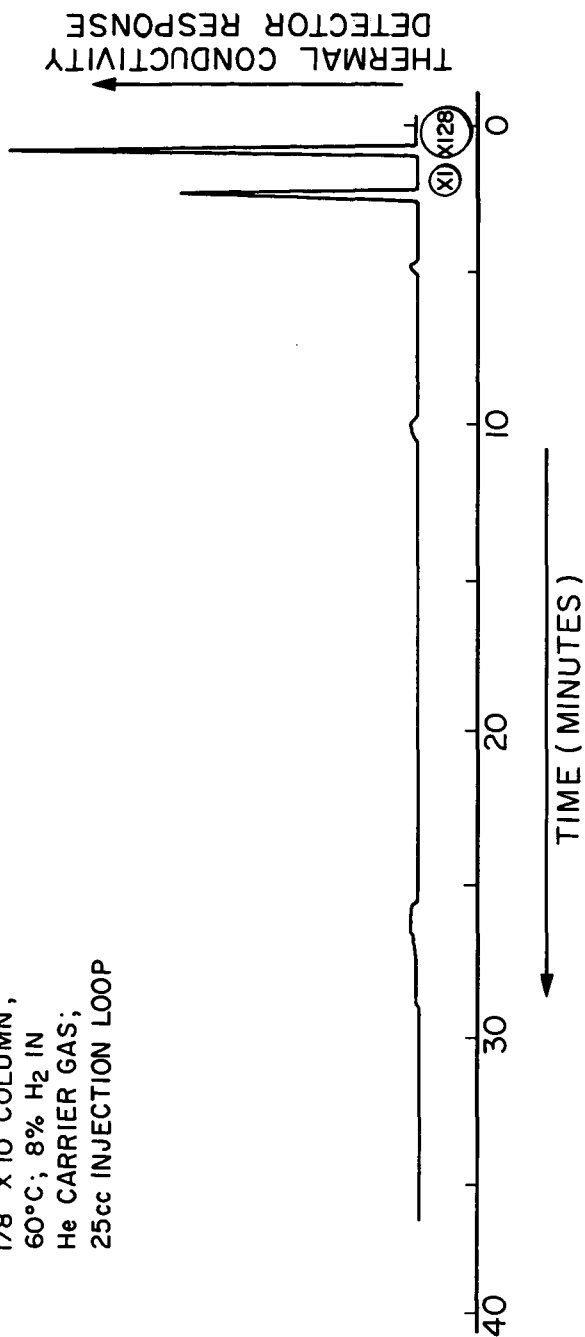
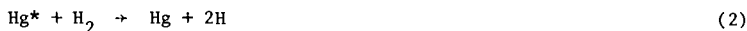


Figure 5

determination of the particle concentration. Swirling coal dust in the reactor zone is visible to acute eyes and is inferred readily by light scattering when He-Ne laser beam is directed through the reactor. A coarse (and, probably, high) estimate of the particle concentration can be made if one assumes that 0.01% of the coal is dispersed in the flowing H_2 at any given time; making this admittedly poor assumption, we calculate 6×10^6 coal particles/cc in the reactor. This suggests about Avogadro's Number of collisions per second between atomic H and coal dust, and the yields suggested in Figures 2 to 4 are consistent with the formation of 10^{14} - 10^{15} product molecules per second. This suggests a collision efficiency of the order of 10^{-9} to 10^{-8} which is below the 10^{-7} value observed by Snelson⁸ for graphite; the estimated coal particle concentration must be far too high and/or the profile of atomic hydrogen not uniform across the reactor. Based on the overall product yield estimates and the actinometry for the entire reactor, the product efficiency per hydrogen atom must be in the 10^{-2} to 10^{-3} range. Clearly, further experimentation, especially product identity and quantification, is required to decrease the uncertainty in the yield per H atom.

Examination of Figures 2, 3, and 4 shows that the gas chromatographic traces are extremely similar for the hydrogenation products from Illinois No. 6, Pittsburgh Seam, and Utah-Emery coals. Although all three are indeed bituminous coals, they are physically very different and one would be surprised if they had identical surface compositions. The "fingerprints" do show subtle differences, but in view of the uncertainties just discussed, one is struck more by their similarity than anything else. (At this writing, only a few of the peaks have been identified. It is hoped that GC-MS identification will be made on every peak this summer.) Either the surface structures which can be "cracked off" by H atoms at 185°-200°C are the same for these three coals or all the products represented by peaks have common precursors which are liberated from the coals in the experiment, e.g., BTX and naphthalenes. Worth mentioning is one experiment in which He carrier gas was used instead of H_2 . Only very small yields of benzene (20 minute elution time) and the product with 35-minute retention time were found in the traps, presumably photo-detached from the coal surface. The yields were far too small to account for all the other products by hydrogen atom cracking of these compounds. Blank experiments using H_2 but leaving the ultraviolet lights off gave no detectable products in an hour. While considerable experimentation remains to be done, the similarity of the products from the three bituminous coals suggest the following mechanism:



⁸A. Snelson, A.C.S. Div. Fuel Chem. Proc. 18, 101 (1973).

In other words, the similarity of the product distributions from the different bituminous coals is proposed to be a result of the similarity of secondary H atom cracking of the product precursors from reaction (3) under the identical reactor conditions, rather than an indication that these three coals, with different histories and different physical properties, have surfaces that are similar. At this point, the only likeness in surface that can be inferred is the ability of H atoms to liberate the hydrogenation precursors from the surface of Illinois #6, Pittsburgh Hi-Seam, and Utah-Emery bituminous coals. Reaction (3) must be similar in rate and reaction products to account for the similarity of Figures 2, 3, and 4. Kinetic information about reaction (4) is appearing⁹⁻¹⁰ and should aid in the interpretation of future experiments involving more uniform concentrations.

Finally, the failure of Wyoming-Wyodak coal to react under identical conditions must be attributed to a slowness of reaction (3). A greater diversity of products from a sub-bituminous coal might have been expected since its organic structures had been subjected to less stringent coalification conditions. Since Figure 5 looks remarkably similar to results from experiments early in this program using Illinois #6 coal at ambient temperature, one might expect a greatly enhanced ESR spectrum such as was observed then. That is, a result of H atom bombardment is the production of nonvolatile free radicals. Further work is clearly warranted.

Nonetheless, it has now been demonstrated that photo-produced H atoms do interact with the surface of bituminous coals at 200°C to yield C₂ to C₈ hydrocarbons. However, the authors feel that further experiments, some altering the steady state H atom concentration and adding suspected precursors, are required to elucidate the mechanisms. Also, an accurate method for determining coal particle concentrations in the photoreactor needs to be found before reliable rate data can be forthcoming. Finally, other sub-bituminous coals need to be examined to see if the Wyodak results, reproduced several times, are common to this rank of coal. Whether H atoms will prove an effective coal surface probe remains to be proven. These preliminary results are encouraging in some respects.

ACKNOWLEDGMENTS

We wish to thank Dr. Fred Radd, Continental Oil Company, who enthusiastically encouraged us to begin coal research, and Mr. Ed Obermiller, CONOCO Coal Development, for both encouragement and the coal samples. Last, but certainly not least, we thank E.R.D.A. for a research grant that supported these experiments.

⁹P. Kim, J. Lee, R. Bonnano and R. Timmons, J. Chem. Phys., 59, 4593 (1973).

¹⁰A. Amano, O. Horie, and W. Hanh, Int. J. Chem. Kinetics 8, 321 (1976).

Enthalpy Measurements on a Syncrude from a Western Kentucky Coal

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ABSTRACT

Enthalpy measurements over the range 65 to 700 F and 100 to 1500 psia were made on a coal-derived liquid using a Freon 11 reference calorimeter. The coal liquid was produced from a western Kentucky coal using the Char-Oil-Energy-Development (COED) process, and was analyzed by the Bartlesville Energy Research Center (BERC/RI-75/12, November, 1975) prior to the measurements.

INTRODUCTION

Thermodynamic property research is justly recognized as invaluable by process and design engineers in the petroleum, chemical, and allied industries. Calorimetric measurements of specific heats or enthalpies, pressure-density-temperature measurements, and phase equilibrium determination, for pure fluids or complex mixtures, are all essential in the optimum design of both physical and chemical processing units.

Coal-derived liquids are a new and vital class of industrial compounds, but have thermodynamic properties that are largely unknown and, presently, unpredictable. The objective of this research is to measure one of the most important thermodynamic properties, the enthalpy, for representative coal-derived liquids over the pressure and temperature regions most likely to be encountered in both liquefaction and processing systems.

The research program is divided into three major areas:

- (1) design, construction, and evaluation of a freon boil off calorimeter for temperatures of 70 to 700°F and pressures to 2000 psig,
- (2) enthalpy measurements on samples of well-defined coal-derived liquids, and
- (3) preparation of engineering correlations for the measured enthalpy data, and comparison with representative data for petroleum and petroleum fractions.

The work reported here is one part of item 2, that is a complete set of enthalpy measurements on a whole (unfractionated) sample of liquid derived from a western Kentucky coal by the COED process.

RESULTS AND DISCUSSION

The liquid used in this work was analyzed by the ERDA Bartlesville Energy Research Center, and the results of their work are available. (G. P. Sturm, Jr., P. W. Woodward, J. W. Vogh, S. A. Holmer, J. E. Dooley, "Analyzing Syncrude from Western Kentucky Coal," BERC/RI-75/12).

The samples used in the calorimetric are from the same lot used by BERC in its characterization studies. The sample was prepared by filtering with Whatman, quality number 1, filter paper before being charged to the system. The enthalpy of the sample was measured along four different isobars (100, 500, 1000, 1500 psia) with the calorimeter inlet temperature varying over the range of 122-705°F. The data are presented in the accompanying table and figures.

The outlet temperature was corrected to the base of 65°F using the heat capacity at this temperature as found from the measured enthalpy vs. temperature curve ($CP = 0.44 \text{ Btu/lb}^\circ\text{F}$). This correction never amounted to more than 0.3 Btu/lbm. The outlet pressure was corrected to a reference of 1 atm. using the Kesler-Lee correlations (Lee, B. I. and Kesler, M. G., *AIChE Journal*, 21, 510 (1975); Kesler, M. G. and Lee, B. I., *Hydrocarbon Processing*, 55, No. 3, 153, (1976)). The pressure corrections are shown in the table.

From the figures it can be seen that for the Western Kentucky syncrude the enthalpy was not a significant function of pressure at high pressures (500 to 1500 psia) where the sample was essentially a liquid at all temperatures. At the lowest pressure of 100 psia where significant vaporization occurs at higher temperatures, the enthalpy is greater at lower pressures (100 psia versus 500 psia).

During the enthalpy measurements, what appeared to be thermal cracking was often observed at pressures above 500 psia and at inlet temperatures above 600°F. The cracked fluid foamed into the collection tube, appeared to be less viscous and changed to a lighter color. The foaming was believed to be the result of a large volume of gas produced by cracking of the sample. An obnoxious odor was also associated with the cracked sample. The cracked-sample enthalpy measurements were higher than the values for the uncracked material possibly due to vapor entrainment. One possible explanation for the cracking is a catalytic effect due to the stainless steel wall of the preheater bath coil. Several modifications were tried in order to correct the problem, including replacing the coil, and more gradual preheating of the oil without much success. A major difficulty is the apparent randomness of occurrence of the cracking. On some runs, the sample cracks and foaming is observed while on others it does not. Several operations are under consideration which could reduce or eliminate decomposition, including hydrogen sulfide flushing of the coil to poison catalytic surface sites, and deaeration of the sample after every run to prevent oxidation reactions. However, until some more definitive conclusions can be drawn, our present operating policy at high temperatures is to complete runs until foaming and sample decomposition occurs. At such time, the system is drained and refilled with fresh sample.

Gas chromatograms of the sample in the system were taken periodically. Chromatograms of the uncracked material showed the same characteristic peaks; however, those of the cracked sample showed small compositional changes in the low temperature boiling range.

ACKNOWLEDGEMENTS

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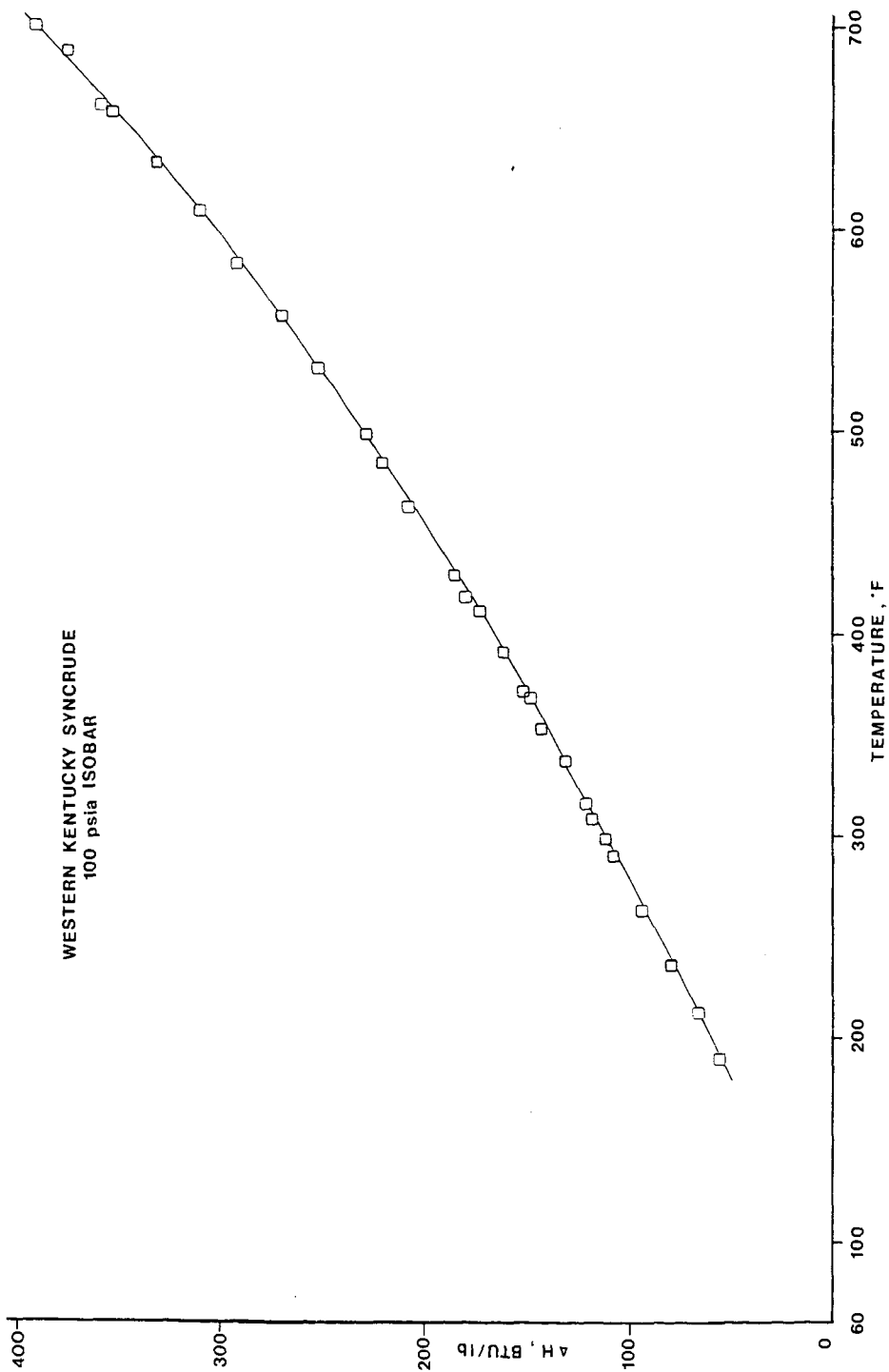
The coal-derived liquid sample used in this work was furnished by Mr. C. J. Thompson, Bartlesville Energy Research Center.

WESTERN KENTUCKY SYNCRUDE ENTHALPY DATA

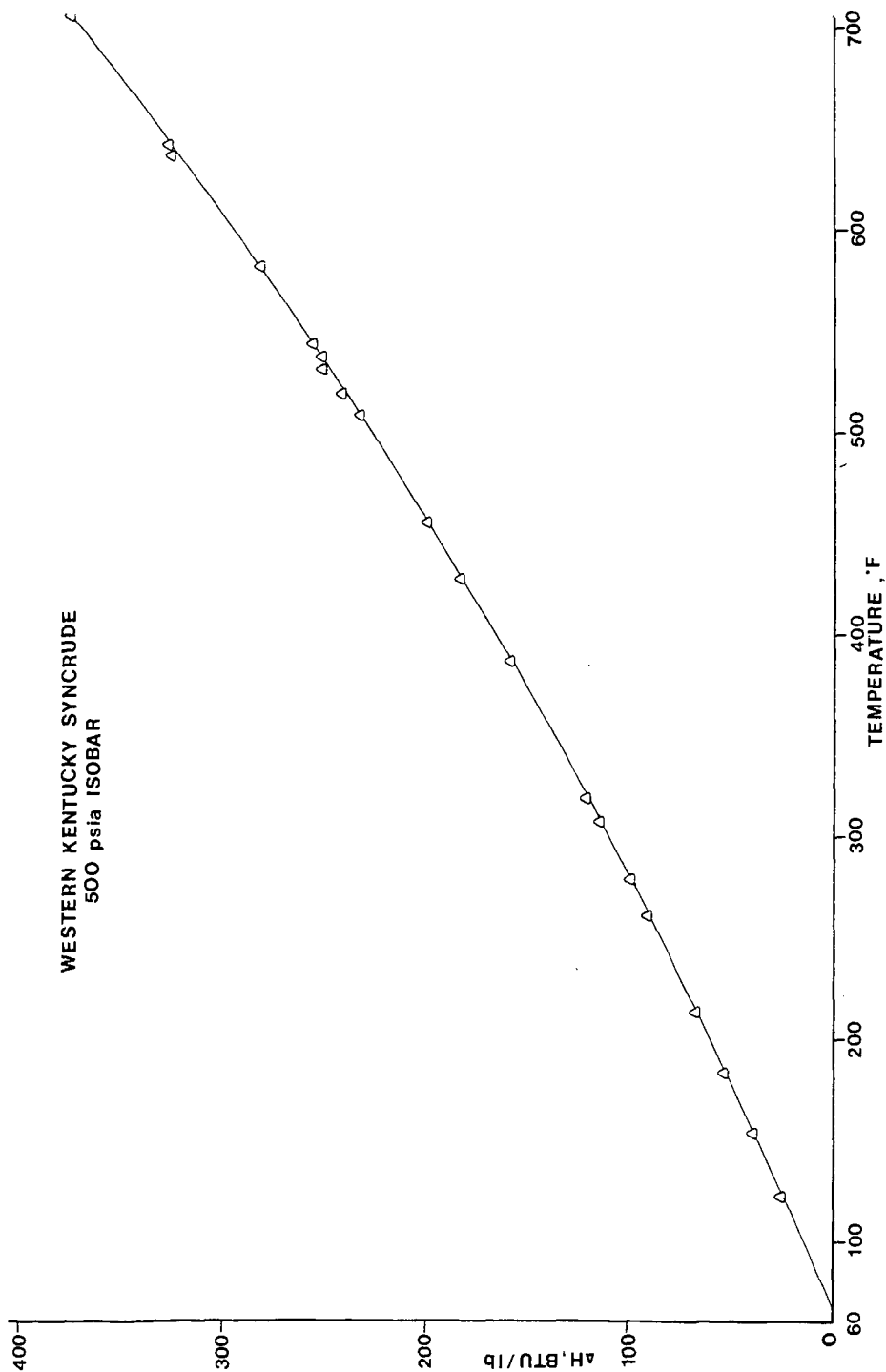
Run No.	Temperature, of Inlet	Pressure, Inlet	psia, Out	ΔH experimental Btu/lb	Pressure Correction Btu/lb	ΔH corrected Btu/lb
1	190.1	106	20	55.7	-0.005	55.7
2	213.4	105	20	65.3	-0.005	65.3
30	237.1	106	20	78.5	-0.005	78.5
29	264.1	105	20	92.5	-0.005	92.5
28	290.6	105	20	107.1	-0.005	107.1
3	298.7	102	27	110.7	-0.012	110.7
27	308.9	132	56	119.1	-0.040	119.1
4	316.3	101	26	121.3	-0.011	121.3
5	337.2	101	27	132.7	-0.012	132.7
7	352.4	104	37	142.6	-0.022	142.6
23	367.3	100	21	148.6	-0.006	148.6
8	371.2	105	38	151.1	-0.022	151.1
9	390.7	104	38	161.6	-0.023	161.6
10	411.1	103	30	173.0	-0.014	173.0
24	418.2	100	20	179.5	-0.006	179.5
11	429.5	103	33	184.9	-0.018	184.9
12	462.0	103	22	207.0	-0.007	207.0
14	483.7	105	30	220.2	-0.014	220.2
15	498.8	101	21	227.7	-0.006	227.7
16	531.6	102	22	251.2	-0.007	251.2
17	556.9	102	21	269.3	-0.006	269.3
18	583.6	102	21	290.7	-0.006	290.7
19	608.9	106	21	308.5	-0.006	308.5
20	633.9	104	22	331.4	-0.006	331.4
26	657.9	105	32	354.2	-0.016	354.2
21	662.0	104	23	358.4	-0.008	358.4
22	689.1	100	20	376.3	-0.005	376.3
25	700.9	104	32	391.0	-0.017	391.0

WESTERN KENTUCKY SYNCRUDE ENTHALPY DATA

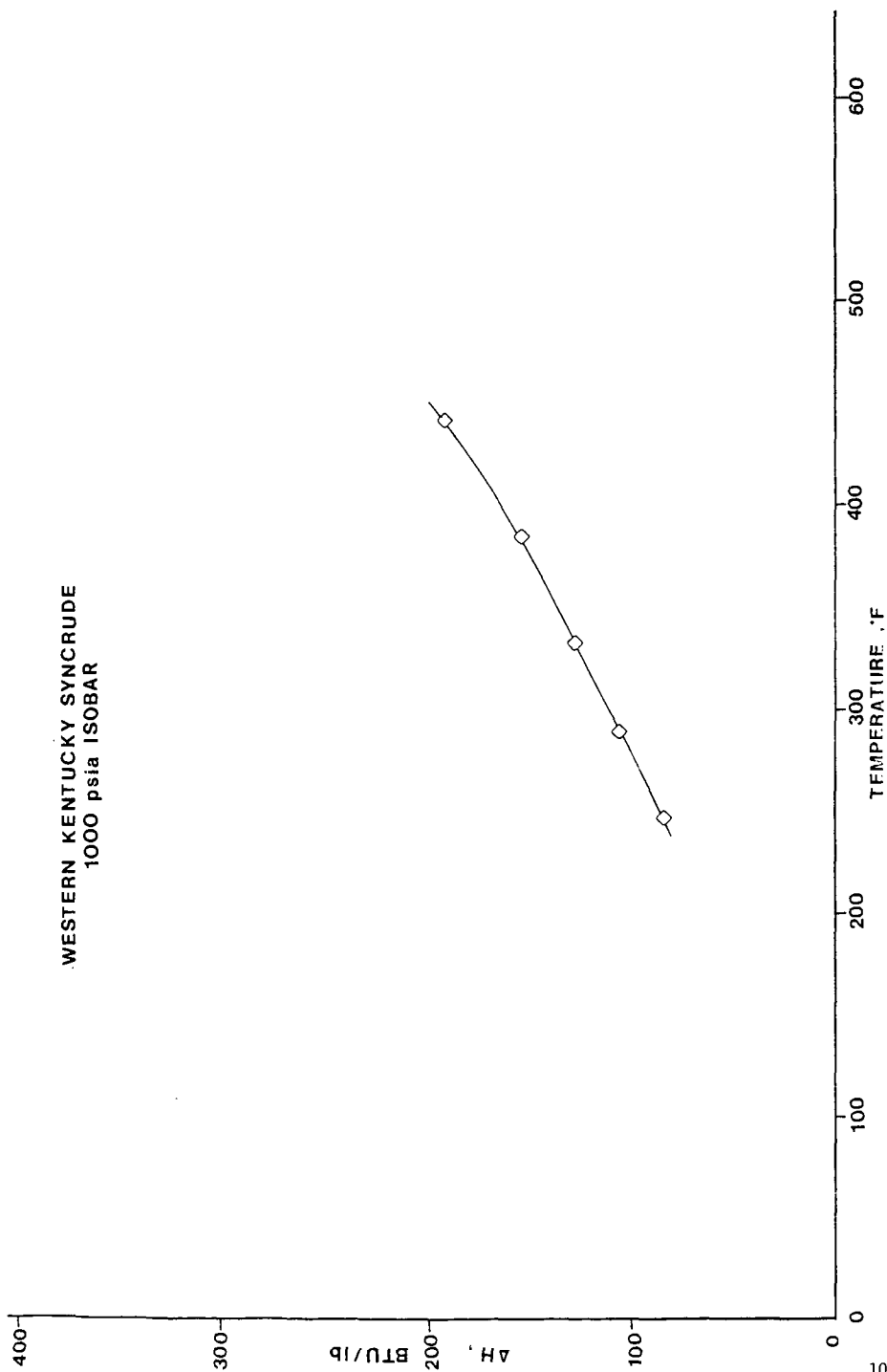
Run No.	Temperature, °F Inlet	Pressure, Inlet	psia Inlet	psia Out	ΔH experimental BTU/lb	Pressure Correction BTU/lb	ΔH corrected BTU/lb
40	122.0	500	346	25.1	-0.32	24.8	
39	154.4	502	379	39.4	-0.35	39.0	
38	183.6	499	378	52.9	-0.35	52.5	
37	213.3	498	279	66.9	-0.25	66.6	
36	261.5	503	384	90.9	-0.36	90.5	
35	280.2	507	415	99.7	-0.39	99.3	
34	306.2	505	416	115.0	-0.39	114.6	
33	307.0	505	417	114.5	-0.39	114.1	
41	319.6	500	424	121.0	-0.40	120.6	
42	387.6	504	424	159.1	-0.39	158.7	
64	427.9	494	369	182.6	-0.34	182.3	
43	455.8	505	423	199.1	-0.39	198.7	
45	507.7	500	408	232.6	-0.38	232.2	
49	518.1	508	438	241.8	-0.41	241.4	
44	531.1	508	424	251.4	-0.39	251.0	
50	537.2	495	436	251.7	-0.41	251.3	
46	544.1	498	394	256.9	-0.37	256.5	
47	582.3	498	405	282.7	-0.38	282.3	
66	636.7	498	419	326.0	-0.39	325.6	
65	641.8	500	397	327.0	-0.37	326.6	
67	705.4	495	418	376.5	-0.39	376.1	
55	246.7	996	911	83.7	-0.86	82.8	
54	288.9	995	913	106.3	-0.87	105.4	
56	332.7	1003	920	127.3	-0.87	126.4	
57	384.2	1000	921	156.3	-0.87	155.4	
58	441.8	1001	922	192.7	-0.87	191.8	
68	268.8	1492	1379	95.9	-1.32	94.6	
62	344.6	1501	1411	141.2	-1.35	139.8	
63	345.7	1498	1411	135.3	-1.35	133.9	
69	391.3	1490	1386	162.7	-1.32	161.4	
61	415.2	1498	1439	174.7	-1.37	173.3	
59	471.8	1498	1437	205.7	-1.37	204.3	
60	472.3	1498	1435	209.4	-1.37	208.0	
70	541.3	1487	1368	255.5	-1.30	254.2	
71	608.8	1486	1382	301.2	-1.32	299.9	
72	640.0	1482	1386	324.1	-1.32	322.8	
73	676.6	1494	1408	355.4	-1.34	354.1	
74	693.1	1487	1408	367.6	-1.34	366.3	



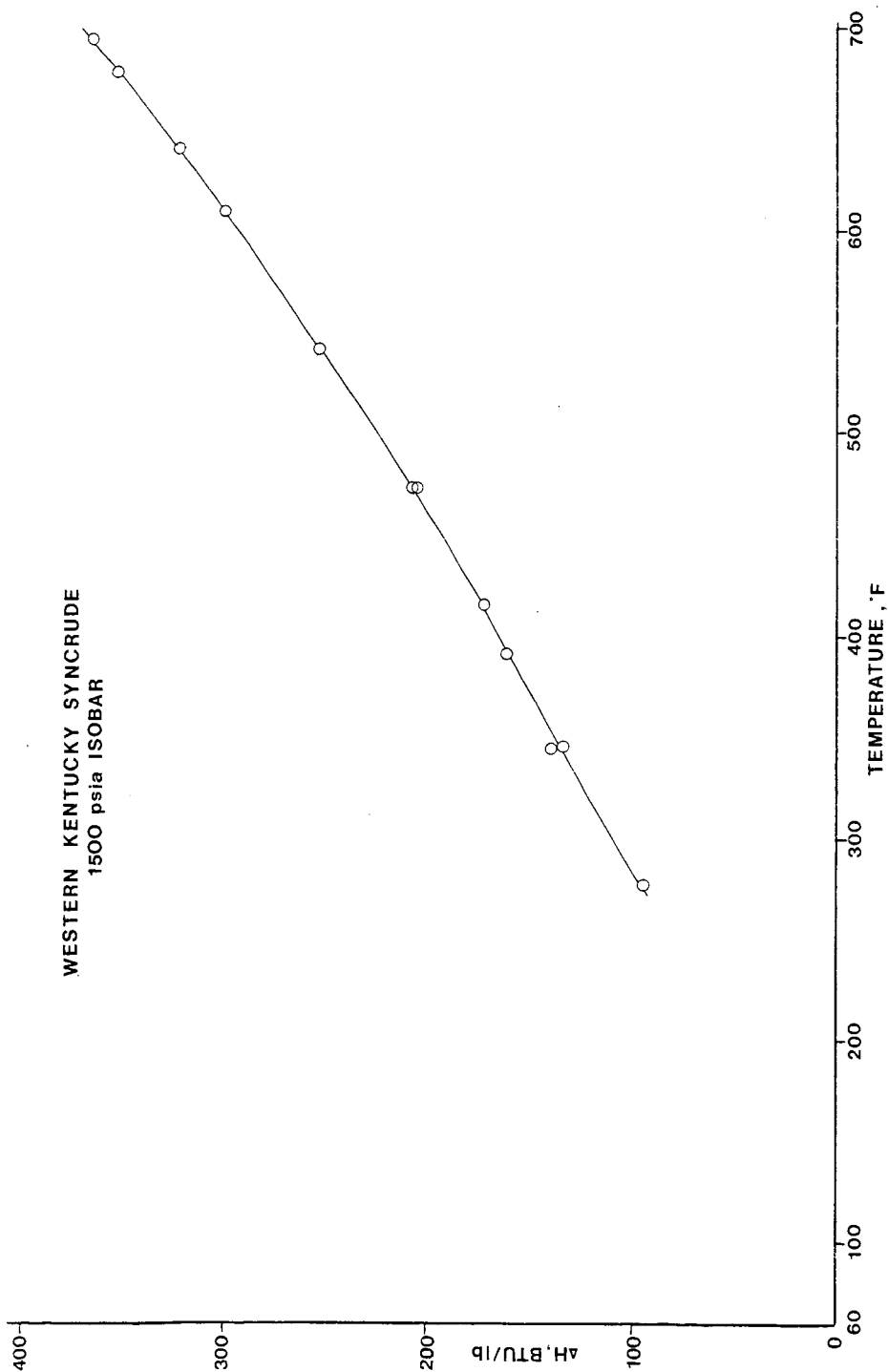
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500 psia ISOBAR



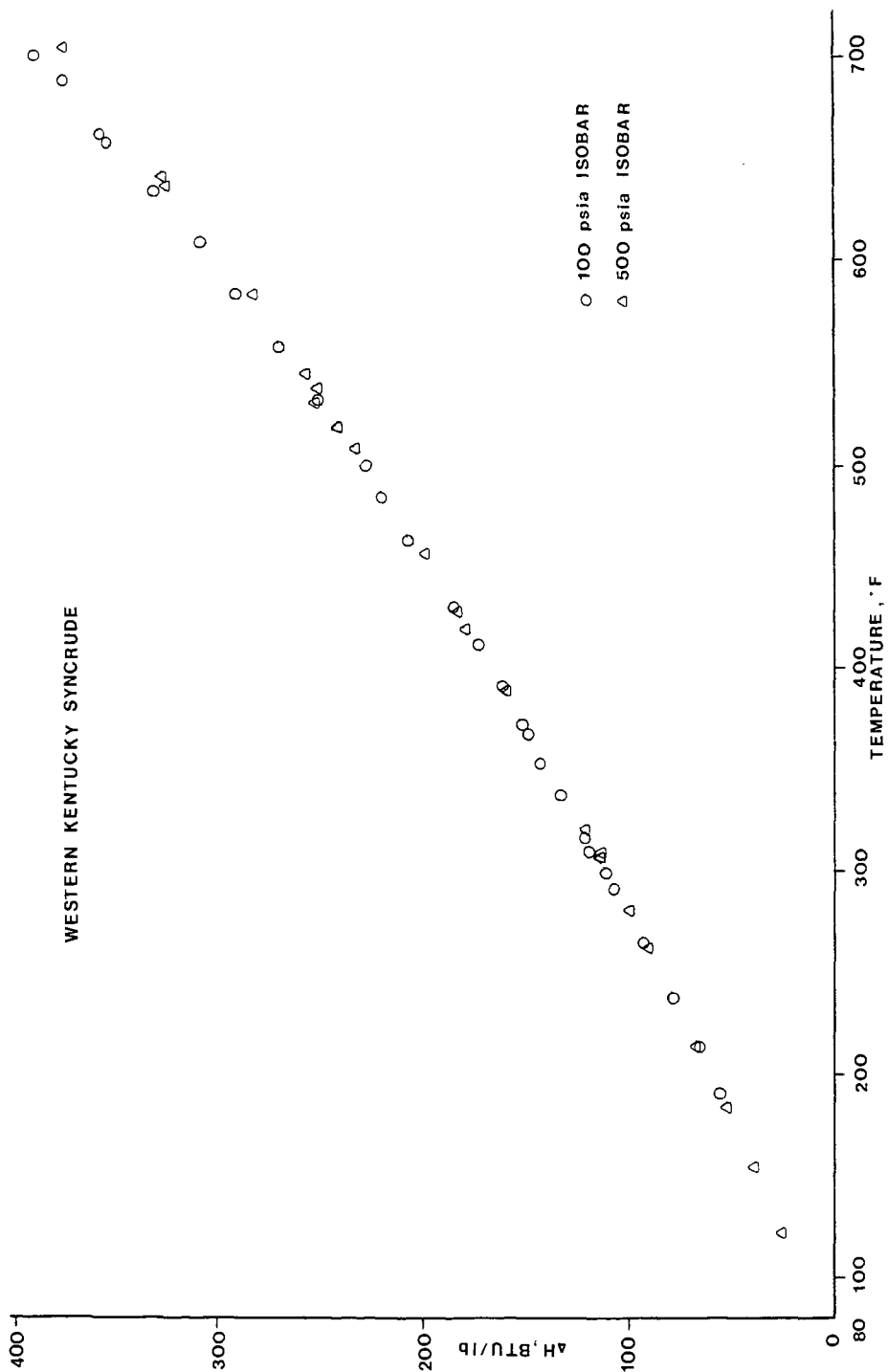
WESTERN KENTUCKY SYNCRUDE
1000 psia ISOBAR



WESTERN KENTUCKY SYNCRUDE
1500 psia ISOBAR



WESTERN KENTUCKY SYNCRUDE



HOMOGENEOUS CATALYTIC HYDROGENATIONS OF COMPLEX CARBONACEOUS SUBSTRATES

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Hydrogenation of unsaturated organic compounds with homogeneous catalysts has been known and practiced for some time. Such hydrogenations have been of both an academic and commercial interest. Some of the more extensively studied catalysts include $\text{Co}(\text{CN})_5^{3-}$ (1), $\text{RhCl}(\text{P}\phi_3)_3$ (2), $\text{Ir}(\text{CO})\text{Cl}(\text{P}\phi_3)_2$ (3,4), $\text{IrH}(\text{CO})(\text{P}\phi_3)_3$ (3,4), $\text{OsHCl}(\text{CO})(\text{P}\phi_3)_3$ (3,4) and Ziegler-type catalysts (5). These catalysts, with the exception of the Ziegler-type, have not been observed to hydrogenate aromatics. Infact, very few homogeneous catalysts have been reported that will hydrogenate aromatics. Wender, *et al.* (6) have shown that polynuclear aromatics are partially hydrogenated with $\text{Co}_2(\text{CO})_8$. Efimov, *et al.*, (7,11) have observed rapid hydrogenation of polynuclear aromatics in the presence of a rhodium complex of N-phenylanthranilic acid (NPAA), formulated as $(\text{RhNPAA})_2$. This rhodium catalyst is more active than the dicobalt octacarbonyl and shows a greater hydrogenation activity toward polynuclear aromatics than the Ziegler catalyst. Holly *et al.* (15) investigated the use of this rhodium complex and other homogeneous catalysts for coal liquefaction, concluding that such catalysts do not appear to offer a viable route to coal liquefaction.

Here we report the results of homogeneous catalytic hydrogenation of complex unsaturated substrates including coal and coal-derived materials.

HYDROGENATIONS

Using organic soluble molecular complexes as catalysts, a number of hydrogenations of various organic substrates were performed. These include a Hvab coal, solvent refined coal (SRC) and COED pyrolysate. The analysis of these feed materials are contained in Table I. The hydrogenations were carried out in a 300 cc stirred autoclave by mixing coal with carrier solvent containing solubilized catalyst under prescribed conditions. Upon completion of the run the gases were measured and analyzed. The solid carbonaceous residue was separated from carrier solvent by filtration, then thoroughly washed with benzene and finally dried in a vacuum oven.

TABLE I. Analysis of Feed Materials

	Coal (a)		SRC	COED	Hydrogenated Coal
	As Received	Vacuum Dried			Run 25
Moisture	1.1	0.0	0.0	0.0	1.8
Ash	14.5	14.7	0.3	0.1	27.0
H	4.8	4.6	5.6	7.3	4.4
C	68.8	68.3	87.7	85.0	55.0
O	6.0	6.1	4.0	7.2	5.9
N	1.2	1.2	2.2	1.1	0.2
S	4.6	4.6	0.5	1.3	4.0

(a) Both samples were -200 mesh.

All catalysts except the Ni-Ziegler are commercially available and were used as such without further purification. The Ni-Ziegler was prepared under a nitrogen atmosphere by reacting 4 moles of triethylaluminum with 1 mole nickel naphthenate in completely anhydrous n-heptane. The activity of this catalyst was first tested with benzene before proceeding to more complex substrates. Hence, 10 ml benzene were hydrogenated in 40 ml n-heptane containing 4×10^{-3} moles of the Ni-Ziegler catalyst for 1 hour at 150°C and 1000 psig H₂ (ambient temperature). Even though the hydrogenation covered a 1-hour period the autoclave pressure rapidly dropped to 650 psig once 150°C was reached, signaling rapid hydrogenation of the benzene. Liquid product analysis by gas chromatography revealed 99% conversion of the benzene to cyclohexane.

Hydrogenation conditions and results for coal and coal derived materials are summarized in Table II. The change in atomic hydrogen-carbon ratio (Δ) is the principal criterion for comparing catalyst activity and extent of hydrogenation. Since no attempt has been made to account for the lighter hydrocarbons that were removed with the carrier solvent by filtration the hydrogenation criterion is very conservative. This value has been obtained by subtracting the experimentally determined atomic hydrogen-carbon ratio of carbonaceous substrate from that of the product. The carbon-hydrogen analysis was performed on a Perkin Elmer model 240 elemental analyzer. Since a small amount of unremoved solvent in the product can seriously effect the interpretation of results, extreme precaution was taken to ensure its complete removal. This was accomplished by washing with a volatile solvent followed by vacuum drying with a nitrogen bleed at 110°C for at least 24 hours. In order to check thoroughness of solvent removal a dried sample showing H/C of 1.10 was further dried and reanalyzed. There was essentially no change in the H/C (i.e., 1.10 versus 1.09).

It is apparent from Table II that the Ni-Ziegler catalyst is more active than Co₂(CO)₈, Ni[(PhO)₃P]₂(CO)₂ and Fe₃(CO)₁₂. In Run 25 a Δ of 0.148 for the Hvab coal was observed over a 2-hour reaction time at 200°C and 2770 psig. This change in atomic H/C ratio from hydrogenation corresponds to a hydrogen usage of only 0.85% (w/w) of coal. Even in Run 36 where a Δ of 0.291 was effected at 200°C and 1300 psig H₂ after 22 hours only 1.7% (w/w) H₂ is consumed in the hydrogenation. These hydrogenations may be compared to Run 31 where a slight decrease in Δ , -0.003, was observed in the hydrogenation of the Hvab coal with no catalyst for 2 hours at 300°C and 2880 psig. In contrast to these hydrogen consumptions about 2% H₂ (w/w maf coal basis) is used in the SRC process, 2.5% in Synthoil and 4% for H-Coal.

Homogeneous catalytic hydrogenations were also conducted on solid products from the SRC and COED coal liquefaction processes. The analyses of these substrates are contained in Table I. Upon examination of the hydrogenation results summarized in Table II it becomes apparent that the ease of hydrogenation under these homogeneous catalytic conditions is SRC > COED > Hvab, although some reservation must be made since the hydrogenations were not made under identical conditions. That the coal-derived substrates are more readily hydrogenated than the coal is not too surprising since they are liquids at reaction temperatures (>200°C) and quite soluble in carrier solvent permitting effective catalyst-substrate interaction. Diffusional resistances to hydrogenation are also expected to be less for these materials than the solid coal.

TABLE II. Summary of Homogeneous Catalytic Hydrogenations of Carbonaceous Substrates

Run No.	Catalyst/Feed ^a /Solvent	Temperature/ Pressure ^d /Time ^b	H	C	At.H/C	Δ(atomic H/C) ^c
31	No catalyst/15g C/decalin	300/2880/2	4.64	68.6	0.806	-0.003
17	14 mmole Co ₂ (CO) ₈ /30g C/decalin	200/2950 ^e /2	4.69	67.4	0.829	0.020
21	7 mmole Co ₂ (CO) ₈ /15g C/decalin	300/3080 ^e /2	5.16	69.0	0.891	0.082
20	7 mmole Co ₂ (CO) ₈ /15g C/decalin	400/3400 ^e /2	5.26	71.8	0.873	0.064
18	13 mmole Fe ₃ (CO) ₁₂ /30g C/decalin	200/2830 ^e /2	4.56	65.9	0.824	0.015
19	7 mmole Ni[(PhO) ₃ P] ₂ (CO) ₂ /15g C/ decalin	200/2720 ^e /2	4.94	70.7	0.833	0.021
25	7 mmole Ni-Ziegler/15g C/decalin	200/2770/2	4.48	55.8	0.957	0.148
36	8 mmole Ni-Ziegler/15g C/heptane	200/1300/22	5.88	63.6	1.10	0.291
38	8 mmole Ni-Ziegler/10g SRC/THF	200/1200/23	7.29	77.1	1.13	0.377
40	5.7 mmole Ni-Ziegler/17.2g COED/THF	200/3850/21	8.28	74.8	1.32	0.290

a Feed materials include: Consolidation coal (C), 4.64%H, 68.3%C, At.H/C = 0.809; Solvent Refined Coal (SRC), 5.55%H, 87.7%C, At.H/C = 0.753; FMC pyrolysate (COED), 7.32%H₂, 85.0%C, At.H/C = 1.03.

b Variables temperature, pressure and time reported as °C, psig and hr., respectively.

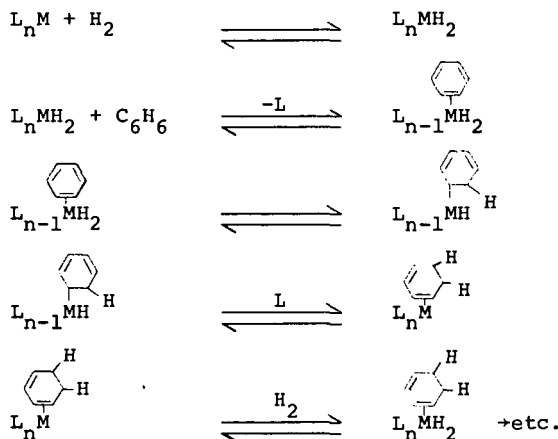
c Δ , is the change in atomic H/C ratio between substrate and product.

d Pressures are those at reaction temperature and due to hydrogen and solvent unless otherwise stated.

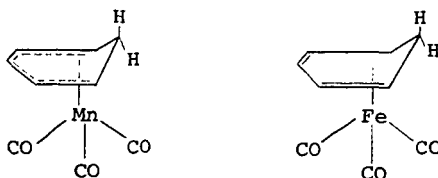
e Gas composition of 25% CO, 75% H₂, used in hydrogenation.

Product gas analysis on each experimental hydrogenation run revealed predominantly reactant gases. In Runs 17, 18, 19, 20 and 21 the product gas consisted of $\geq 98\%$ H_2 and CO , while Runs 25, 31, 36, 38 and 40 showed at least as great a concentration of hydrogen. Except for Run 20, CO_2 and CH_4 contributed $\leq 0.2\%$ to the gas balance. The gas composition of Run 20 was different from the others in that low but noticeable concentrations of light hydrocarbons including CH_4 , C_2H_6 , and C_3H_8 were found. The observed light hydrocarbons in this run are undoubtedly due to the higher temperature ($400^\circ C$ versus $\leq 300^\circ C$) employed, which was high enough to affect hydrogenolysis. The gas analysis of Runs 25, 36, 38 and 40 employing the Ni-Ziegler catalyst were unique in that appreciable concentrations (1 to 2%) of ethane were observed. The ethane is attributed to loss of ethyl groups from the Ni-Ziegler catalyst or decomposition of excess triethylaluminum which was used in its preparation.

Even though there is no kinetic data to support a proposed mechanism for the observed homogeneous catalytic hydrogenation of aromatics the following mechanism is consistent with the chemistry of analogous systems. In this proposed mechanism L represents coordinated ligands and solvent and M is the transition metal. This proposed mechanism depicts that generally accepted for the hydrogenation of olefins (including cyclohexene) by a number of group VIII metal complexes.



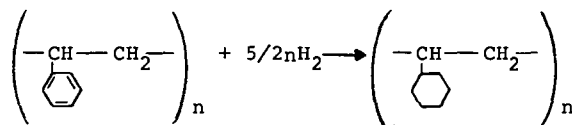
We know for instance that molecular hydrogen will undergo oxidative addition reactions with a number of transition metal complexes as shown in the first equation (12). The metal migrations during hydrogenation may occur through a π -allyl complex. Finally, intermediates similar to those postulated in this mechanism have been supported by chemical evidence and include the two following compounds (13):



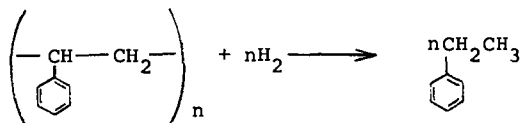
Even though the above mechanism has been written with benzene as the substrate it is relatively easy to write analogous mechanisms for yet more complex aromatic substrates.

PRODUCT CHARACTERIZATIONS

The products from the hydrogenation of the coal and coal derived materials were all solid glossy black materials at room temperature, except in Run 20 where the temperature reached 400°C and a black viscous liquid was obtained. The carbon and hydrogen analyses of these hydrogenation products are contained in Table II. With respect to these complex carbonaceous substrates hydrogenation is often falsely taken to be synonymous with liquefaction. The polymeric structure of coal (8,9) implies that complete saturation with hydrogen would not alter its physical state. An appropriate analogy would be the hydrogenation of polystyrene to produce the solid saturated polymer



Even though polyethylene has an H/C ratio of 2.0, it is also solid. Hence with respect to coal liquefaction, undoubtedly the hydrogenolysis reactions and not hydrogenation are responsible for converting the solid to a liquid by conventional processing schemes. The liquefaction that occurred in Run 20 was undoubtedly due to hydrogenolysis as a consequence of the high temperature (400°C) employed. Again using polystyrene for analogy, the hydrogenolysis may be represented by the following reaction in which the product ethyl benzene is clearly a liquid.



Coal hydrogenolysis has been contrasted with its hydrogenation by carrying out a material balance estimation on the Synthoil process as shown in Table III. These results show that one net result of catalytic hydrogenolysis is a decrease in the product (char + crude oil) H/C ratio (0.765 versus 0.883), despite the addition of 9000 scf H₂ per ton of coal (maf). The decrease in the H/C ratio is a direct consequence of the hydrogenolysis reaction which breaks structural bonds in the solid substrate and adds hydrogen to the fragments. Hence, a large hydrogen consumption is seen in removing oxygen and sulfur from the coal as H₂O and H₂S, respectively. Considerable hydrogen is also consumed by light hydrocarbon gases (C₁ - C₃) as a result of hydrogenolysis reactions. On the other hand, hydrogen consumed by hydrogenation goes directly to increase the substrate H/C ratio. This is why the H/C ratio is high for the amount of hydrogen consumed in the homogeneous catalytic hydrogenations. Of course, from a practical viewpoint it is highly desirable, if not necessary, to at least remove the sulfur which is invariably accompanied by oxygen removal and light hydrocarbon gas production.

Complete hydrogenation of the unsaturated carbon-carbon bonds in the complex carbonaceous substrates is estimated to result in an H/C

ratio of at least 1.5. The maximum value we have obtained is 1.32 for the COED pyrolysate. The failure to obtain more extensive hydrogenation may be due to the catalyst's inability to activate the more complex aromatics. Also, a portion of the substrate's unsaturation is undoubtedly very facile and a portion is very inert toward hydrogenation. As noted earlier, the Ni-Ziegler very rapidly hydrogenates mononuclear aromatics but is much more sluggish toward the polynuclear aromatics. For example, at 1000 psig H_2 , phenol is 92% converted to cyclohexanol in 0.2 hours at 150°C in the presence of 5 mole % Ni-Ziegler catalyst, while only 12.5% naphthalene is converted to decalin in 18 hours at 210°C in the presence of 2.5 mole % Ni-Ziegler (5). The more complex polynuclear aromatics, such as phenanthrene and pyrene that are contained in coal along with the heteropolynuclear aromatics such as indoles and dibenzothiphenes will undoubtedly be even more sluggish toward hydrogenation.

TABLE III. Synthoil Material Balance

Materials Charged	lb-moles	lb
Coal (a) (atomic H/C = 0.883)	2000	
C	1117.90	1416
H	104.20	105
O	22.50	360
S	3.00	96
N	7.50	105
Hydrogen (b) (H)	50.04	50.5
		<u>2050.5</u>
Materials Out		
C ₁ -C ₃ Hydrocarbons (c)	100	
C	6.52	78.3
H	21.53	21.7
Heteroatoms	467.8	
H ₂ O (d)	21.25	382.8
H ₂ S (e)	2.5	85.0
Product (f) (atomic H/C = 0.765)	1482	
C	111.4	1338
H	85.3	86
O	1.2	20
S	0.5	16
N	1.6	22
		<u>2049.8</u>

(a) maf basis.

(b) 50.04 lb-moles H equivalent to 9000 scf H_2 .

(c) Amount to 5 wt% of maf coal charged with estimated composition of 60% C₁, 30% C₂ and 10% C₃.

(d) 340 lb O + 42.8 lb H.

(e) 80 lb S + 5.04 lb H.

(f) Crude oil + char.

Another possible cause of low hydrogenation levels is the inaccessibility of catalyst to substrate. This is anticipated to be more of a problem for coal than for coal-derived products, due to their differences in physical properties, particularly pore size distributions and solubility in carrier solvent. The moderate to high solubility of the coal-derived materials will undoubtedly enhance catalytic hydrogenation over the relatively insoluble coal in a carrier solvent. The coal itself having an extensive pore structure will undoubtedly contain a significant number of micropores that are too small for access of the catalyst (14).

To obtain information on the reactivity of the solid hydrogenated product, thermogravimetric analyses were run and compared to those of the unhydrogenated coal. The results are shown in Figure 1 for hydrogenation products of Runs 25 and 36 as well as the parent coal. These differential thermograms were all recorded with a duPont model 900 analyzer on 19-23 mg samples under a high-purity argon atmosphere at 20°C/min heating rate, from ambient to 800°C. Although the sample from Run 25 had an H/C of 0.148, greater than the parent coal, there is no qualitative difference in their differential thermograms except for the small amount of moisture devolatilized from the parent coal at about 125°C. This type of thermogram is typical of many that have been reported for different ranks of coal (10). In sharp contrast, the sample from Run 36 which had an H/C increase of 0.291 over the parent coal reveals considerable structure in its differential thermogram. In addition to the major peak at about 475°C which was also observed for the coal and sample from Run 25, two additional peaks were observed at considerably lower temperatures--one at 360°C and the other at 275°C. The volatile matter from this sample was 54% (ash-free basis) while that from Run 25 and the parent coal was 42% and 37% respectively (ash-free basis).

It is not surprising that the sample from Run 36 showed more structure in its thermogram and a larger amount of volatile matter production than the parent coal since it does have a significantly greater hydrogen content than the parent coal. What is somewhat surprising is that the sample from Run 25 acted very similar to the parent coal during thermolysis even though its H/C ratio lies between that of product from Run 36 and the parent coal. The hydrogenation in Run 36 is apparently extensive enough to saturate key unsaturated groups in coal leading to decreased thermal stability. It is generally recognized that cleavage of saturated groups is much more facile than unsaturated groups under thermolysis conditions.

To project the yield of liquid product from the thermogravimetric analysis we have assumed that a linear relationship exists between the percent volatile matter and liquid yield. This implies that if a coal is 25% volatilized and yields 10% oil then 35% devolatilization of this coal after pretreatment such as hydrogenation will yield $0.35/0.25 \times 10\% = 14\%$ oil. Using this approximation one can readily estimate that prehydrogenation of the coal in Run 36 has increased yield of oil by 46% over the unhydrogenated coal upon pyrolysis. In practical terms this means that prehydrogenation could be used to significantly increase the yield of liquids from coal by pyrolysis. For instance, the oil yield from the COED process (16) which uses multiple stage pyrolysis to produce gases, liquids and char would be increased from 1.5 bbl/ton to about 2.2 bbl/ton.

HYDROGENOLYSIS

A hydrogenolysis experiment was conducted with the Hvab coal and its hydrogenated product under identical experimental conditions. The analysis of these -200 mesh feed materials was reported in Table 1. Hydrogenolysis was carried out in the previously described 300 cc magne drive autoclave. In the hydrogenolysis of Hvab, 10.0 g were charged to the autoclave along with 30.0 g (32 ml) tetralin and 0.5 g -100 mesh Co-Mo catalyst (Harshaw HT-400 containing 3% cobalt oxide and 15% molybdenum dioxide on alumina). In the hydrogenolysis of the prehydrogenated coal from Run 25 the same quantity of carbonaceous feed and tetralin were charged, but no catalyst was added. After materials were charged, the autoclave was purged twice with high-purity hydrogen and then pressurized with hydrogen to 1500 psig. Experimental hydrogenolysis conditions were 0.5 hour at 400°C, 2700 psig (1500 psig H₂ ambient) and 300 rpm. The autoclave was brought up to reaction temperature and cooled after the designated reaction time as rapidly as possible. It required about 30 minutes to reach 400°C from ambient and 10 minutes to cool from 400°C to 60°C. However, the time required to heat from 200°C to 400°C and cool from 400°C to 200°C was only about 2 minutes; i.e., the time spent at temperatures sufficiently high to potentially contribute to hydrogenolysis was significantly shorter than the overall heat-up and cool-down time.

Once the run was completed and the temperature had cooled to ambient the experiment was worked up according to the diagram in Figure 2. The gas volume was measured with a wet test meter and its composition determined by gas chromatography. The liquid and solid products were emptied into a tared extraction thimble whence the filtrate from the thimble was collected and saved. The autoclave was rinsed with benzene into the same extraction thimble. The solids were then extracted with the rinse benzene for 8 hours in a soxhlet apparatus whence the extraction thimble was vacuum dried and weighed. The benzene solution from the extraction was combined with the previously saved tetralin-laden filtrate. To this solution was added a three-fold excess of pentane, to precipitate asphaltenes which were then separated by filtration and vacuum dried. This filtrate was then vacuum distilled (~25 mm Hg, 40-80°C) to remove the pentane and benzene from the tetralin soluble product (light oil). The yields of the various fractions obtained by following this procedure are all summarized on a maf charge basis in Table IV for the Hvab coal and the prehydrogenated coal.

The tabulated results (Table IV) for the hydrogenolysis of the coal and hydrogenated coal clearly indicate a significant difference in their product yields. The yield of gas and light oil was greater for the hydrogenated than the nonhydrogenated coal (38% and 49.0% versus 31% and 48.6%). Perhaps even more significant is the lower asphaltene yield observed for the hydrogenated sample (3.0% versus 10.3%). The overall conversion was essentially the same for both samples (90 versus 89%) and there was little difference in their product gas compositions.

In examining the differences between these two hydrogenolysis experiments one is reminded that while a Co-Mo catalyst was used with the coal, there was no addition of catalyst to the hydrogenated coal. However, the hydrogenated coal did contain nickel that was apparently deposited on the coal from the Ni-Ziegler catalyst during the homogeneous catalytic hydrogenation. This nickel undoubtedly participated as a catalyst in the hydrogenolysis of the sample. So in essence, we are comparing the hydrogenolysis of this hydrogenated sample containing

nickel with the Hvab coal to which was added a conventional Co-Mo catalyst. An analysis* of the nickel content in the hydrogenated coal revealed 1.2% Ni which can be compared to 5% Co-Mo catalyst in the Hvab coal. Since the nickel catalyst was apparently decomposed on the hydrogenated coal sample it almost certainly had better catalyst-substrate contacting than the Co-Mo which was mixed with the Hvab coal. This in itself could account for the higher hydrogenolysis yields of gas and light oil and lower asphaltenes than with the Co-Mo catalyst. In addition, nickel catalysts generally show higher gas yields under

TABLE IV. Hydrogenolysis Experimental Results

	Hvab Coal	Hydrogenated Coal Run 25
Reaction Conditions		
feed, g	10.0	10.0
tetralin, g	30.0	30.0
catalyst, g	0.5	none
temperature, °C	400	400
pressure, psig	2660	2770
time, hr	1/2	1/2
Conversion, %	90.0	88.9
Product Yields, %		
gas	30.8	38.0
oil	58.8	52.1
light oil	48.6	49.0
asphaltenes	10.2	3.0
char	10.3	9.9
Gas Composition, mole %		
H ₂	91.2	87.7
CO ₂	0.5	0.4
C ₂ H ₄	trace	trace
C ₂ H ₆	2.4	2.6
O ₂	trace	0.3
N ₂	0.5	2.5
CH ₄	4.1	3.9
CO	0.1	0.2
C ₃ H ₈	1.3	2.3
C ₄ H ₁₀	0.2	0.1

hydrogenolysis than supported Co-Mo catalysts. Finally, the hydrogenated sample is expected to produce higher yields of gases and light oils and lower asphaltenes under hydrogenolysis simply because it has been hydrogenated.






* The analysis of the hydrogenated sample was performed by first ashing the sample at 850°C in a muffle furnace. This revealed 27.0% ash. The ash was then digested in hot aqua regia solution and filtered. The filtrate was then diluted with water and analyzed for nickel by atomic adsorption spectroscopy to give 1.2% Ni in the hydrogenated sample.

In an attempt to better define the nature of the liquid product from the hydrogenolysis of these two samples their light oil fractions were subjected to gas chromatographic-mass spectral analysis. The more prominent components of the tetralin soluble fraction (light oil) from hydrogenolysis of the two samples were analyzed on a Hewlett-Packard (HP) 5980A quadrupole mass spectrometer with a HP 5710A GC and HP 5934A data system. Chromatography was performed on a 6-foot SP 2250 column temperature programmed from 80 to 250°C at 8°C/min using He carrier at 40 ml/min. Mass spectrometry was conducted with electron impact at 60 electron volts. Additional chromatography of the light oil from each sample was performed on an HP 5830A GC equipped with an HP 18850A terminal at the previously described run conditions.

A typical chromatogram of these samples is shown in Figure 3 along with retention times while Table V contains the mass spectral identification of the more prominent components of both samples. Upon comparing the chromatograph data their similarity is particularly striking. When the solvent (tetralin) is subtracted from both samples as has been done in tabulating the area percent in Table VI we quickly realize that only a few of the more than 22 integrated peaks account

TABLE V. G. C. Mass Spectral Analysis of Light Oil

G. C. Retention Time, Area %		Mass Spec Assignments	
Hvab Coal	H ₂ -Hvab Coal		
0.59 , 18.59	0.58 , 16.02	benzene	
0.93 , 0.44	0.93 , 0.52	toluene	
1.19 , 0.15	1.19 , 0.20		
1.60 , 0.67	1.59 , 1.32	xylene	
2.15 , 0.35	2.17 , 0.52	xylene	
2.99 , 0.46	2.97 , 0.68	C ₃ -benzene	
4.41 , 2.06	4.39 , 2.03	decalin	
5.73 , 8.10	5.78 , 10.37	C ₄ -benzene	
7.44 , 20.47	7.51 , 22.74	1-methylindane	
8.38 , 0.93	8.41 , 1.04		
12.32 , 40.54	12.35 , 40.61	naphthalene	
13.15 , 0.80	13.17 , 0.49	Methyl-tetrahydronaphthalene	
14.07 , 0.50	14.12 , 0.14		
14.65 , 0.82	14.67 , 0.60		
15.30 , 0.65	15.33 , 0.29	methyl-naphthalene	
16.13 , 0.42	16.17 , 0.05		
17.38 , 1.17	17.18 , 0.54	C ₂ -tetralin	
17.87 , 0.32	17.88 , 0.08		
18.51 , 0.68	18.53 , 0.10		
---	18.95 , 0.03		
19.54 , 0.31	19.47 , 0.10		
20.34 , 0.04	20.40 , 0.12		
20.90 , 0.04	20.93 , 0.12		
21.86 , 0.05	21.87 , 0.07		
22.87 , 0.29	22.89 , 0.28		
24.25 , 0.12	24.28 , 0.27	Methyl-biphenyl	
25.15 , 0.66	25.20 , 0.52		
26.12 , 0.00	26.19 , 0.02		
28.00 , 0.18	28.07 , 0.12		

for the majority of the sample. In fact, there are only five compounds, all with two or greater area percent, that account for greater than 90 area percent of the entire sample. These compounds are common to each sample and include the following in descending order of abundance: naphthalene () > methyl indan ( -CH₃) > benzene (), C₄-benzene ( -C₄H₉) > decalin (). Of these five compounds the first three account for a least 80% of the light oil in each sample. The broadness of many of the chromatogram peaks, particularly those at the longer retention time, is a good indication that they consist of more than one component. Hence, the number of chemical compounds actually in the light oil sample is probably at least twice the number of integrated GC peaks.

UTILITY

Even though homogeneous catalytic hydrogenation has had considerable practical utility in the hydrogenation of specialized chemicals such as certain fats, oils and pharmaceuticals, its economic and technical utility in processing carbonaceous feedstocks such as coal, oil or their derived intermediates is very uncertain. We have seen that prehydrogenation of coal can significantly increase the amount of liquids obtained by pyrolysis compared to the unhydrogenated coal. It has also been shown that the hydrogenolysis of prehydrogenated coal produces less asphaltene and more light oil and gas than the catalytic hydrogenolysis of the parent coal. Finally it was shown that homogeneous catalytic hydrogenation can effectively increase the atomic hydrogen to carbon ratio of the carbonaceous materials including coal and materials derived from coal by pyrolysis and solvent refining.

Although the amount of experimental data generated here in support of homogeneous catalytic hydrogenation is infinitesimal in regard to that needed for a sound technical judgment concerning its utility in the area of fuels processing, there is a clear indication that the approach has merit. The extrapolation of the experimental data indicates that homogeneous catalytic hydrogenation has considerable potential as a preliminary processing step for carbonaceous materials such as coal, and possibly oil shale and tar sands for increasing the atomic H/C ratio over conventional methods. The derived benefit from such a unit operation aside from the addition of hydrogen to these hydrogen-deficient materials is to increase the yield and quality of the products over what is now obtainable by conventional processing techniques at such mild conditions. Yet another potential application of homogeneous catalytic hydrogenation is as an intermediate step in fuel processing or conversion schemes in which the H/C ratio is increased to produce a superior quality product. Finally, potential applications of homogeneous catalytic hydrogenation are foreseen in the area of basic research studies where it is used as an analytical tool or technique for investigating complex carbonaceous substrates.

Much of the impetus behind contemplating the use of homogeneous catalysts lies in the prospects of reducing temperature and pressure required for conversion, increasing reaction specificity and obtaining the most efficient use possible of the active metal component. In some instances of homogeneous catalytic hydrogenation, all these prospects have been realized. I think that it is reasonable to expect that homogeneous catalysts will eventually be developed that are capable and effective in hydrogenolysis reactions of carbon-carbon bonds. This indeed would be an extremely significant break-through with respect to coal liquefaction.

The major technical drawback to the use of homogeneous as well as heterogeneous catalysts is connected to their recovery from processing streams and poisoning. Since catalysts are extremely expensive, processing materials as a result of their manufacturing costs and cost of their component constituents only small losses can be economically tolerated. In homogeneous catalytic hydrogenation Run 25 where 7 mmole of Ni-Ziegler catalyst was employed per 15 g coal, the cost of nickel alone at zero recovery (i.e., 54.8 lb/ton coal) would amount to about \$110/ton coal hydrogenated. If the cost of the triethylaluminum and the carboxylate of nickel are taken into consideration the cost of catalyst materials alone is estimated to exceed \$150/ton coal hydrogenated. Clearly, in order to contemplate such a use of these catalysts, they must either be recovered or used in a much reduced concentration or preferably both. Even though no attempts were made at catalyst recovery or use of reduced amounts in this study it was found that the hydrogenated coal in Run 25 contained 1.2% Ni. This figures to be 31% of the nickel used in the homogeneous catalytic hydrogenation. The remaining 69% of the nickel catalyst apparently remained in the carrier solvent, which in practice would be recycled. Obviously, even higher catalyst recovery is necessary to promulgate its economic viability.

That catalysts can be used effectively and economically in bulk chemical processes is amply demonstrated in the hydrocarbon processing industries. Although these catalysts have been for the most part heterogeneous, homogeneous catalysts have found a home in at least two notable areas. One is the use of Ziegler catalysts in coordination polymerization and the other is in the hydroformylation process. These two examples show that the technical and economic problems so often associated with the use of homogeneous catalysts in industrial processes can be overcome.

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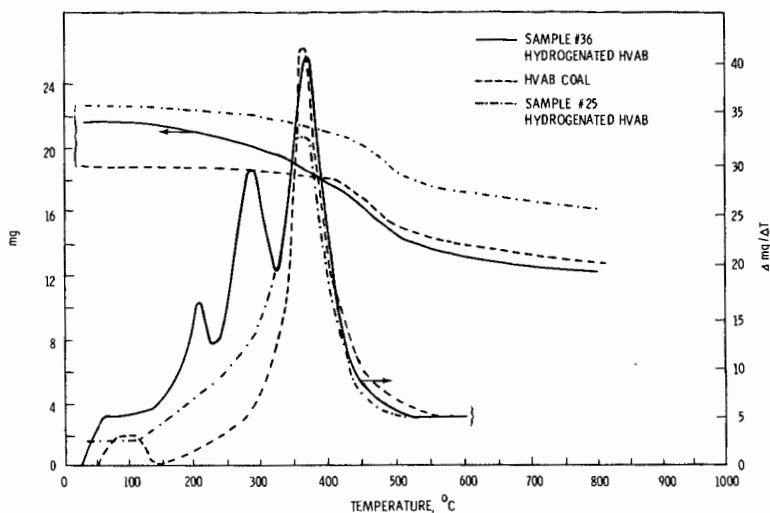


FIGURE 1. Thermograms and DTG of Coal and Hydrogenated Coal

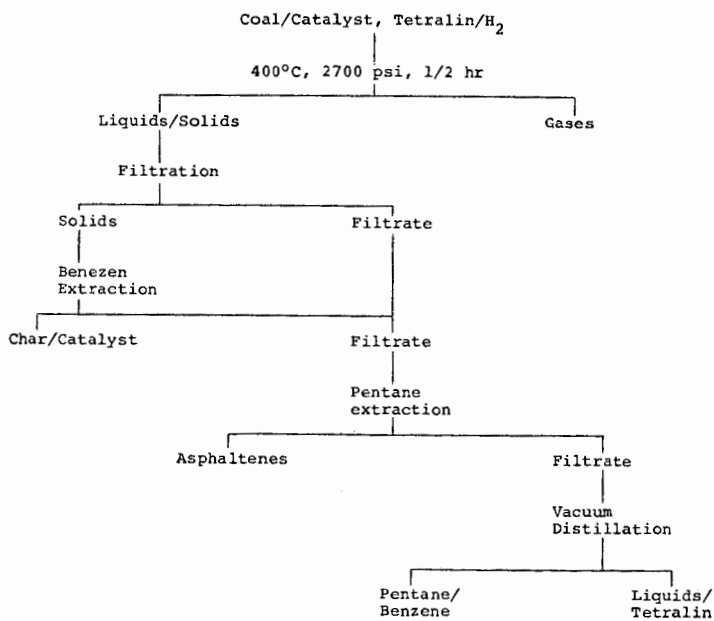


FIGURE 2. Schematic for Workup of Hydrogenolysis Experiments

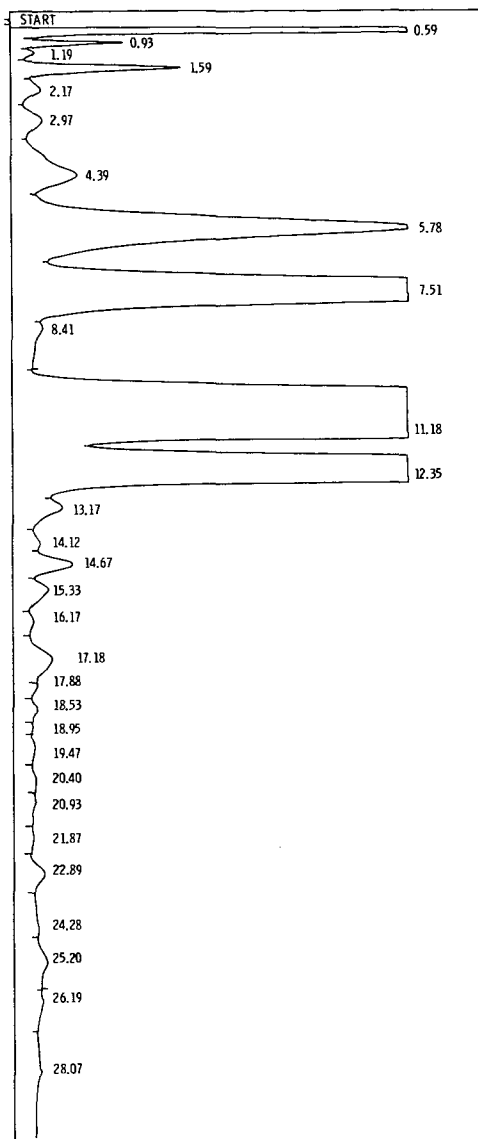


FIGURE 3. Gas Chromatogram of Light Oil from Hydrogenolysis of Hydrogenated Hvab Coal

The Selectivity of Coal Minerals as Catalysts in Coal Liquefaction and Hydrodesulfurization

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Introduction

Certain coal minerals are well-known to catalyze liquefaction and hydrodesulfurization in coal conversion processes (1,2,3,4). It is generally understood in connection with liquefaction processes that heating coal to temperatures in the range of 350°C and higher produces free radicals by thermal bond rupture. These free radicals are then stabilized by abstracting a small entity such as a hydrogen atom from some source. The source may be hydrogen chemically interacted with the catalyst (coal minerals or other added catalysts), hydrogen on the hydroaromatic portion of a hydrogen donor solvent or perhaps hydrogen on the hydroaromatic portion of coal (5,6,7). Some studies of catalytic hydrodesulfurization of coal-solvent slurry systems have been done with various commercial catalysts (8,9,10). Instead of voluminous work with good hydrogenation and hydrodesulfurization catalysts, little attention has been paid to coal mineral catalysis. Coal mineral catalysis might be important in the Solvent Refined Coal (SRC) process, in which solid boiler fuel is produced through mild or little hydrogenation of coal - probably mainly through dissolution of coal.

To better understand the importance of coal mineral catalysis in the SRC process, this work presents comparative results of the rates of hydrogenation and hydrodesulfurization of coal/oil slurries under different reaction conditions and in the presence of different coal minerals. The selectivity of coal minerals such as reduced iron and SRC residue (Wilsonville SRC pilot plant) for hydrodesulfurization as opposed to hydrogenation has been determined based on product distribution (oil, asphaltene and preasphaltene), sulfur content of each product and analyses of liquid products. The rate limiting steps, or the reaction step most affected by catalytic activity of coal minerals have also been examined.

Experimental

Equipment

All autoclave studies were performed in a commercial 300 cc magnedrive autoclave (Autoclave Engineers). The autoclave was equipped with a stirrer, thermowell, furnace, cooling coil, gas inlet and sampling lines. Coal-tetralin systems were studied in a small tubing-bomb reactor ($\frac{1}{2}$ " O.D. stainless steel tube with 0.035" wall thickness). Under air atmosphere about 16 ml reactors were used with Swagelok caps on both ends. Hydrogen gas was introduced into a smaller tubing-bomb reactor (about 13 ml), sealed with Swagelok cap on one end, through 1/16" tube which was connected to the pressure indicator to read pressure change during reaction. Varian gaschromatographs (Model 1800) were used for analysis of oil fraction. A Leco sulfur determinator (Model 532) was used for analysis of sulfur in each product.

Materials

Creosote oil (Allied Chemical Company) and light recycle oil (LRO) used in this study were obtained from Southern Services, Inc. The creosote oil has a carbon-to-hydrogen ratio of 1.25 (90.72% C and 6.05% H), a specific gravity of 1.10 at 25°C, and a boiling point range of 175 to 350°C. The creosote oil consists of 96.1% oil, 3.5% asphaltene, 0.2% preasphaltene and 0.3% pyridine insolubles. The light recycle oil (LRO) contains mainly oil (99.4%) and a little asphaltene (0.6%). The values

were obtained following the solvent extraction scheme, which will be described in the experimental procedure section. The sulfur content is 0.64% in the creosote oil and 0.26% in the light recycle oil (LR0).

Kentucky No. 9/14 mixture (-150+325 mesh, a high volatile bituminous coal) was used in all experiments (67.8% C, 4.9% H, 2.69% S and 12% mineral matter). All coal samples were dried overnight at 100°C and 25 inches Hg vacuum before use.

Co-Mo-Al and representative coal minerals (iron and SRC residue) were obtained and studied as catalysts for the reactions of hydrogenation and hydrodesulfurization. Co-Mo-Al is a commercial catalyst from Laporte Industries, Inc. (Comox 451). Iron is a reagent grade hydrogen reduced iron from Mallinckrodt, Inc. SRC residue was obtained from filter cake from Wilsonville SRC pilot plant (2.48% S). All catalysts were screened to -325 mesh before use. Presulfided Co-Mo-Al was prepared by collection of solid residue after reaction of creosote oil with Co-Mo-Al in the autoclave reactor. Sulfur content is about 2.76%.

Hydrogen and nitrogen gas cylinders (6000 psi grade) were supplied by Linde. The following chemicals were used: benzene (Mallinckrodt, nanograde or Fisher Certified A.C.S.), pentane (Mallinckrodt, nanograde), hexane (Fisher Certified), pyridine (Fisher Certified A.C.S.) and tetralin (J.T. Baker, practical grade).

Procedures

A 2:1 solvent-to-coal weight ratio (40 grams of coal, 80 grams of solvent-LR0 or creosote oil) was charged to the autoclave. In some cases, a 3:1 solvent-to-coal weight ratio was used. The reaction conditions used for most of runs were 410°C, a stirrer setting of 1000 rpm, and an initial hydrogen or nitrogen pressure of 2000 psig. A heat-up rate of about 12 to 20°C per minute was used, thus requiring a total heat-up time of about 30-35 minutes. After two hours of reaction, the autoclave contents were quenched to below 100°C within 15 minutes. Then all reaction products were collected in a container and cooled down to room temperature. Immediately, the products were subjected to analysis following the solvent extraction scheme. Each separated product was collected for sulfur analysis.

Usually 3 grams of coal and 6 grams of solvent (tetralin) were charged to the small tubing-bomb reactor (2.4 grams of coal and 4.8 grams of tetralin under hydrogen atmosphere). The reaction experimental procedures were similar to Neavel's (7). The vertical stirring rate was in the range of 100-500 times a minute. Immediately after reaction for 30 minutes in a fluidized sandbath and cooling down, all reaction products were collected by cleaning with benzene first and then with pyridine, then analyzed following the solvent extraction scheme. Each product was collected for sulfur analysis. The oil fraction was analyzed by gas chromatograph to see tetralin consumption during reaction.

About 9 grams of reaction products from the autoclave reactor or all products from the small tubing-bomb reactor were separated following a conventional solvent extraction scheme with pentane or hexane, benzene and pyridine, as shown in Figure 1. The actual weight of oil fraction was slightly higher than the difference between the original sample amount and the sum of asphaltene and benzene insolubles, indicating some solvent (benzene, hexane or pentane) remaining after rotaevaporation up to about 80-85°C under vacuum. To resolve this, the true value for oil or preasphaltene fraction was chosen as follows:

oil = sample - asphaltene - benzene insolubles

preasphaltene = benzene insolubles - pyridine insolubles

Good reproducibility was obtained with +1% deviation, based on percentage of each separated product (+3% deviation, based on dmmf coal).

Results and Discussion

Liquefaction

It is generally believed that coal liquefaction follows a coal→preasphaltene→asphaltene→oil route, by breaking C-O, C-S, C-C and possibly C-N bonds and stabilizing coal-derived free radicals by hydrogen transfer from hydrogen chemically interacted with the catalyst (coal minerals or other added catalyst), hydrogen on the hydroaromatic

portion of a hydrogen donor solvent or perhaps hydrogen on the hydroaromatic portion of coal (5, 6, 7, 10, 11). The major role of catalyst in liquefaction appeared to be the replenishment of the hydrogen donor solvent in order to maintain the proper level of hydroaromatics (1, 12). The hydrogen atmosphere, the hydrogen donor ability of the solvent and the hydrogenation activity of the catalyst seem to be most important variables among others in liquefaction process.

A series of experiments using the autoclave reactor was performed to evaluate the sensitivity of the rates of hydrogenation and hydrodesulfurization and to a lesser degree, liquefaction of a coal/oil slurry to variations in atmospheric composition (H_2 or N_2), type of solvent (light recycle oil, LRO, or creosote oil), and presence of different catalysts (Table I). The selectivity of different catalysts in terms of overall effect on product distribution (gas, oil, asphaltene, preasphaltene, and pyridine insolubles) was also examined. Creosote oil and LRO were simply assumed to exist as oil after reaction. Creosote oil contains, however, about 3.5% by weight of asphaltene, affecting significantly the oil and asphaltene portions in runs B and D. In runs A, B, C, and D, as to be expected, both liquefaction (based on pyridine soluble degree) and hydrogenation (based on benzene soluble degree) occurred to a larger extent in a hydrogen atmosphere than in an inert nitrogen atmosphere -- the pyridine solubles yield being 35% higher and the benzene solubles yield, 25% higher -- irrespective of the type of solvent used, LRO or creosote oil.

Hydrogen donor species like tetralin and hydrophenanthrene are present in significant amounts in LRO; whereas only trace amounts of these species are present in creosote oil. As a result, LRO is considered to be a much better SRC solvent than creosote oil, which is used as an SRC startup and makeup solvent. Extent of liquefaction and hydrogenation are strongly dependent on solvent characteristics, or type. For example, the pyridine soluble yield was increased by 27% and the benzene soluble yield was increased by 21% -- irrespective of the atmosphere, H_2 or N_2 -- when LRO was used instead of creosote oil.

The results of runs A and E clearly demonstrate the pronounced effect of the presence of presulfided Co-Mo-Al -- a well known hydrogenation catalyst -- on product distribution: the oil fraction is increased by about 76% over that resulting in the absence of the catalysts; the preasphaltene fraction is decreased by about 71%; and the pyridine insoluble fraction is decreased from 12.5% to practically zero percent, with the asphaltene fraction remaining essentially the same. The presence of Fe (run F) and SRC residue (run G) had, on the other hand, a much less pronounced effect on product distribution. Most interestingly, in the presence of Fe the pyridine insoluble fraction decreased to practically zero; and the oil fraction increased by about 27%, with the asphaltene and preasphaltene fractions remaining essentially the same. Within the limits of experimental error, in the presence of SRC residue product distribution remained practically the same. Based on these results, Fe appears to be more effective than SRC residue in accelerating oil and pyridine soluble yields, with both being much less effective than presulfided Co-Mo-Al.

In Table II hydrogen consumption during reaction was compared, based on H_F/H_0 value (the ratio of final hydrogen partial pressure to that in the initial charge at reaction temperature). The justification for using this value to gauge hydrogen consumption was presented in an earlier work (13) in which the kinetics of hydrogenation were described in detail. The presence of SRC residue and coal ash had significant effects on hydrogen consumption, being next to that of presulfided Co-Mo-Al and significantly higher than that of Fe. In fact, the presence of Fe had little, or no effect on hydrogen consumption (H_F/H_0) as compared to that occurring during non-catalytic reaction. Apparently, based on the gas analyses and in light of the above results with regard to product distribution (Table I), the higher hydrogen consumption that resulted in the presence of SRC residue are due partly to higher yields of gaseous products (H_2S , CH_4 , CO_2 , C_2-C_5 , etc.). The results from previously reported (1) catalyst screening studies (Table IV) also support the hydrogen consumption data in Table II. In addition, the results of earlier HPLC analyses of creosote oil after hydrogenation in the presence of different catalysts (Table V)(14) indicated that the degree of hydrogenation was greater in the presence of SRC residue and coal

ash than in the presence of Fe (pyrite). The peak height ratio of tetralin to naphthalene in the gas chromatographic analyses of the liquid products (Table II) indicated a similar trend to that observed in the HPLC analyses (Table IV) and the H_f/H_o values (Table II), that is, that hydrogenation reactions are accelerated significantly more by SRC residue and coal ash than by Fe. In conclusion then, despite the more significant effect of Fe than that of SRC residue on overall product distribution, as was discussed earlier, the presence of Fe during reaction has little effect on hydrogen consumption; whereas that of SRC residue causes a significant increase in hydrogen consumption. Also, apparently based on the results given in Table III, solvent-to-coal ratio has little effect on hydrogen consumption.

Table VI shows the results from a series of runs in which 2:1 coal/oil slurries were reacted in the presence of different concentrations of Fe catalyst. Samples used to perform gas analyses and for determining the sulfur content of the liquid fraction (that fraction which passed through Whatman #51 filter paper) were collected immediately upon completion of the specified reaction period (2 hrs). In agreement with the findings of the other studies discussed earlier, the presence of Fe catalyst did not have an appreciable effect on gas make (CH_4 , CO_2 , and C_2-C_5) or H_f/H_o values. Also, as was observed earlier, Fe served to completely scrub out any H_2S produced.

Table VII shows the results of a set of experiments in which a small tubing-bomb reactor was used. When a vertical agitation rate in the range of 100-500 cycles per minute was used, with an air atmosphere the presence of Fe catalyst did not affect the product distribution. More importantly, even with a hydrogen atmosphere and in the presence of Co-Mo-Al catalyst, the product distribution was not drastically different from that obtained with an air atmosphere and in the absence of the catalyst. This insensitivity apparently is due to the poor mass transfer obtained at this low agitation rate; for with an agitation rate of above 1000 cycles per minute, the product distribution changed significantly, with substantially more hydrogenation occurring. Further reaction studies using the tubing-bomb reactor are currently in progress.

Hydrodesulfurization

As shown in Table VIII the rate of hydrodesulfurization (HDS) of a 3:1 coal/oil slurry was the same in a N_2 atmosphere as that in a H_2 atmosphere when no catalyst was present during reaction. An earlier more detailed study of non-catalytic HDS (13) showed that the rate of HDS is indeed insensitive to not only hydrogen partial pressure but also the concentration of hydrogen donor species in the solvent. However, as shown in both Table I and VIII, in the presence of Co-Mo-Al catalyst the rate of HDS was significantly higher in the presence of a H_2 atmosphere than that in a N_2 atmosphere. In fact, for a 3:1 coal/oil slurry the sulfur content of the liquid reaction products was lower even under a N_2 atmosphere when Co-Mo-Al catalyst was present during reaction. For a 2:1 coal/oil slurry, in the other hand, no detectable lowering in the sulfur content of the liquid products due to catalytic activity under a N_2 atmosphere was observed (Table I and VIII). This insensitivity of HDS reactions to catalytic activity at the lower solvent-to-coal ratio could be due to the rapid depletion of hydrogen donor species that occurs under a N_2 atmosphere. For instance, as shown in Table IX, the degree of conversion of coal to liquids (cresol solubles) under a nitrogen atmosphere was the same after two hours of reaction as that after 15 minutes, presumably because of the rapid depletion of donor species; for, in the presence of a H_2 atmosphere, a significant increase in conversion resulted when the reaction time was increased from 15 minutes to two hours. If the catalyst can serve to accelerate HDS reactions by facilitating the transfer of hydrogen from donor species to active sulfur bearing species, then the concentration of donor species does take on importance, and the observed decrease in catalytic activity with a decrease in the solvent-to-coal ratio should be expected. Further experiments are in progress to ascertain the extent to which HDS catalysts can serve to accelerate reactions in this capacity. The major role of HDS catalysts appears nevertheless to be the acceleration of the transfer of gaseous hydrogen to reactive sulfur bearing

species. Thus, a H_2 atmosphere must be present for a catalyst to be most effective in accelerating HDS reactions.

Apparently from Table II, Fe proved to be about as effective as a desulfurization catalyst as did presulfided Co-Mo-Al. Among the liquid products, Co-Mo-Al was selective in accelerating desulfurization reactions in that it affected the asphaltene fraction the most in both percentage of sulfur ($0.92 \rightarrow 0.50\%$) and absolute weight of sulfur ($0.12 \rightarrow 0.07$ gr). The selectivity of Fe catalyst among the liquid products was not as apparent as that of Co-Mo-Al catalyst.

In an earlier study (13) H_2S was shown to inhibit the activity of HDS catalysts. This inhibition by H_2S could be due to either the blocking of active hydrogenation centers or back reaction by H_2S product. Fe reacts with product H_2S to form non-stoichiometric FeS_{1+x} , and as a result, is a much more effective HDS catalyst than either pyrite or reduced pyrite (Table IV), each of which rapidly form non-stoichiometric FeS_{1+x} during HDS (13). Further evidence of the inhibition of catalytic activity by H_2S is provided by comparing the results given in Table II and IV: during the HDS of a coal/oil slurry in the presence of coal ash too much H_2S was apparently produced for the ash to scrub out (Table II), and because of H_2S inhibition the coal ash was totally ineffective as an HDS catalyst; whereas during the HDS of creosote oil all of the H_2S product was scrubbed out by the coal ash (Table IV), and the coal ash was a very effective HDS catalyst. For similar reasons, as shown in Table II, SRC residue is essentially ineffective as a HDS catalyst. Because of the scrubbing action of H_2S product by Fe then, it is a very effective HDS catalyst. In fact, as shown in Table VI, Fe Catalyst appears to be selective in accelerating HDS reactions more than hydrogenation reactions, in that as its concentration was increased from one to 13.3 percent, sulfur removal increased significantly with little change in hydrogen consumption (H_f/H_0).

Process Application

During startup of the Wilsonville SRC pilot plant it has been observed that mineral matter accumulates in the dissolver until steady state conditions are achieved. This mineral matter has been found to exert some catalytic activity, particularly with regard to liquefaction and hydrogenation reactions. This finding is in complete agreement with the results discussed above. Actual SRC residue obtained from the Wilsonville plant as well as several minerals indigenous to coal and even coal ash, for example, were shown to act as effective hydrogenation catalysts. However, two major disadvantages to the use of SRC residue were observed: 1) it is ineffective as a HDS catalyst; 2) it is not selective in the catalytic activity and contributes to excess hydrogen consumption due to excess gas formation, etc. The results obtained for SRC residue should be indicative of the catalytic behavior of the mineral matter that exists in the SRC dissolver. To illustrate: an appreciable H_2S atmosphere exists in the SRC dissolver during normal steady state operation. Like pyrite, reduced pyrite, and coal ash as well as SRC residue then -- all of which were observed to be ineffective HDS catalysts in a H_2S atmosphere -- indigenous mineral matter does not scrub out H_2S product, and as a result, should not exert a significant catalytic activity for HDS reactions. In addition, the hydrogen consumption required to obtain the typical conversion yields obtained at Wilsonville have been estimated using non-catalytic kinetics to be about one half of that actually required (15). The catalytic activity existed by indigenous coal minerals was suggested to be the major cause of this higher hydrogen consumption.

In contrast to the minerals indigenous to coal, Fe has been shown here to be most attractive as a catalyst for the SRC process: 1) it is an effective HDS catalyst; 2) it is somewhat selective with regard to accelerating hydrogenation reactions, with minimal contribution to increased hydrogen consumption.

Acknowledgement

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Figure 1: Block Diagram for Separation Procedures

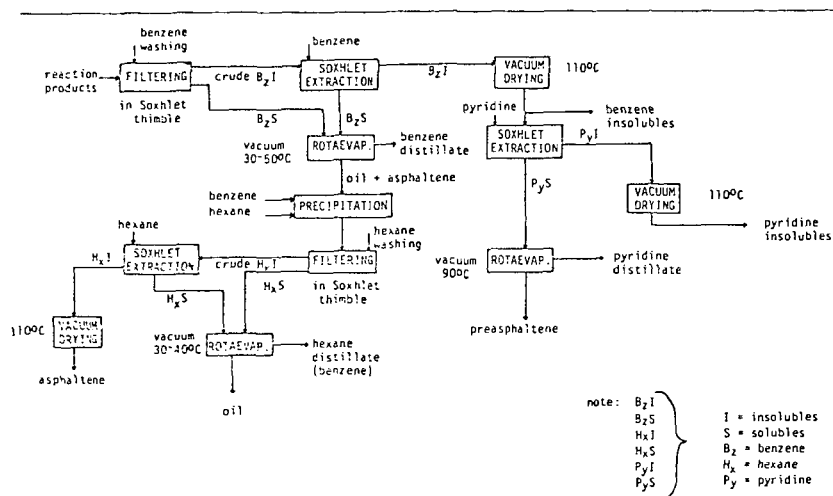


Table 1. Product and Sulfur Distribution by Different Solvent and Catalyst in Autoclave Reactor

solvent/coal = 2, T = 410°C, 120 minutes, 1000 rpm							
runs	A	B	C	D	E	F	G
solvent	LRO	creosote	LRO	creosote	LRO	LRO	LRO
catalyst (14.3%)	-	-	Co-Mo-Al*	Co-Mo-Al*	Co-Mo-Al*	Fe	SRC residue
gas (psig)	H ₂ (2000)	H ₂ (2000)	N ₂ (1000)	N ₂ (1000)	H ₂ (2000)	H ₂ (2000)	H ₂ (2000)
product, %**							
oil	32.6	7.1	16.5	4.0	57.4	41.4	33.0
asphaltene	38.4	42.5	28.7	19.3	37.8	38.5	45.2
preasphaltene	16.6	11.1	8.5	2.3	4.8	19.3	12.8
insolubles	12.5	39.3	46.3	74.4	0.0	0.9	9.1
sulfur, %							
oil	0.31	0.49	0.34	0.51	0.25	0.25	0.31
asphaltene	0.92	0.98	0.89	0.78	0.50	0.75	0.90
preasphaltene	0.55	0.63	0.65	0.99	0.78	0.30	0.63
insolubles	4.07	2.46	2.82	2.42	4.01	4.00	3.82
total sulfur, grams							
reactants	1.28	1.59	1.84	2.14	1.84	1.28	1.78
products (except gases)	0.80	1.03	1.56	1.71	1.32	1.36	1.60
oil	0.28	0.40	0.29	0.42	0.25	0.24	0.29
benzene solubles	0.40	0.55	0.38	0.47	0.32	0.34	0.41
pyridine solubles	0.43	0.57	0.40	0.48	0.33	0.36	0.44

*: presulfided Co-Mo-Al

**: based on dmmf coal and solvent-free

Table II. Effect of Type of Catalyst on Hydrogen Consumption and Rate of Hydrodesulfurization of a Coal/Oil Slurry

solvent (LRO)/coal = 2, T = 410°C, 120 minutes, 1000 rpm

Catalyst	Initial Pressure (1x10 ⁻³ psig)	Final Pressure (1x10 ⁻³ psig)	Partial Pressures (psig)					Sulfur Content Of Liquid Products**	Hf/Ho***Tetralin/Naphthalene Ratio****
			H ₂ (10 ⁻³)	H ₂ S	CO ₂	CH ₄	C ₂ -C ₅		
Co-Mo-Al*	2.00	1.32	0.783	70	48	172	108	0.24	0.42
"	2.02	1.32	0.523	151	97	234	175	0.19	0.28
SRC Residue	2.01	1.52	0.842	41	115	244	132	0.38	0.45
	2.00	1.36	0.739	35	115	206	125	0.37	0.40
	2.02	1.51	0.834	48	132	219	137	0.39	0.44
Coal Ash	2.02	1.38	0.812	23	131	168	106	0.37	0.43
	2.00	1.48	0.919	25	80	190	127	0.37	0.49
	2.01	1.32	0.830	11	57	178	104	0.37	0.44
Fe	2.00	1.48	1.08	0.0	42	136	87	0.24	0.58
	1.99	1.44	1.01	0.0	45	156	92	0.27	0.55
	2.01	1.46	1.02	0.0	45	157	99	0.24	0.55
None	2.28	1.71	1.21	35	49	167	114	0.374	0.57
	1.92	1.59	1.11	37	56	155	95	0.417	0.62
	2.09	1.70	1.25	36	44	135	90	0.350	0.64
	2.02	1.65	1.19	48	53	141	83	0.411	0.63
	2.01	1.54	--	--	--	--	--	0.402	--

* Presulfided Co-Mo-Al

** Liquid products: those that pass through a Whatman #51 filter paper

*** Hf/Ho: the ratio of the final hydrogen partial pressure to the original

**** The peak height ratio in the gas chromatograph analysis of liquid products

Table III. Effect of Catalyst and Solvent (LRO)-to-Coal Ratio on Hydrogen Consumption

T = 410°C, 120 minutes, 1000 rpm

Co-Mo-Al* Catalyst	Solvent-to- Coal Ratio	Initial Pressure (10 ⁻³ psig)	Final Pressure (10 ⁻³ psig)	Partial Pressures (psig)					Hf/Ho**
				H ₂ (10 ⁻³)	H ₂ S	CO ₂	CH ₄	C ₂ -C ₅	
None	3:1	2.02	1.72	1.16	31.3	37.4	280	73	0.62
None	3:1	2.00	1.70	1.34	7.4	41.8	108	68	0.72
15.0%	3:1	2.00	1.229	0.56	127	58	198	144	0.30
15.0%	3:1	2.02	1.360	0.82	54	55	169	118	0.44
None	2:1	2.00	1.48	0.95	50	45	137	93	0.62
15.0%	2:1	2.00	1.320	0.783	70	48	172	108	0.42
15.0%	2:1	2.02	1.320	0.523	151	97	234	175	0.28

*,** same as in Table II

Table IV. Catalyst Screening Runs: Liquid % Sulfur, Final Total Pressure, Final Gas Composition, and Fractional Decrease in Hydrogen Pressure

15 grams catalyst, 100 grams creosote oil, $T = 425^{\circ}\text{C}$,
 $P_i = 3000$ psig H_2 , 120 minutes, 2000 rpm

Mineral	% Sulfur*	Final Total Pressure (10^{-3} psig)	H_2 (10-3)	H_2S	CO_2	CH_4	$\text{C}_2\text{-C}_5$	$\text{H}_f/\text{H}_0^{**}$
None	0.52	2.40	2.13	10.	2.5	64.	18.	0.74
None	0.46	2.42	2.23	7.1	2.0	62.	24.	0.78
Muscovite (-80)	0.39	2.18	1.94	8.5	1.0	51.	20.	0.68
Iron (-325)	0.27	1.98	1.75	< 1.	12.	16.	20.	0.61
Reduced Pyrite	0.36	1.96	1.85	17.	0.4	61.	18.	0.65
Coal Ash	0.23	1.92	1.72	< 1.	1.4	57.	15.3	0.60
Siderite	0.34	1.81	1.61	< 1.	67.	93.	29.	0.56
SRC Solids (-325)	0.32	1.73	1.48	13.	24.	85.	30.	0.52
Co-Mo-Al (-80, +150)	0.02	1.12	0.92	< 1.	1.9	128.	74.	0.32
Co-Mo-Al (-325)	0.02	1.02	0.73	1.7	1.3	138.	79.	0.26

* Liquid products: those that pass through a Whatman #51 filter paper

** H_f/H_0 : the ratio of the final hydrogen partial pressure to the original

Table V. HPLC Analysis of Treated Creosote Oil

Compound	A	B	C	Wt. %	D	E	F
1 and 2-naphthanthrile	0.611	0.458	0.243	trace	0.046	trace	
carbazole	0.423	0.366	0.418	0.386	0.443	0.526	
naphthalene	8.92	7.49	6.55	4.16	4.01	4.17	
1-methylcarbazole	0.106	0.084	0.059	0.067	0.102	trace	
1-methylnaphthalene	5.23	4.56	3.14	3.13	2.33	2.08	
2-methylnaphthalene	8.00	6.21	7.63	5.42	4.61	4.37	
acenaphthene	6.28	4.15	1.56	2.38	2.24	2.08	
fluorene	5.22	5.02	3.78	3.62	3.64	4.55	
disbenzothiophene	1.27	0.888	0.720	trace	0.576	0.622	
phenanthrene	12.4	9.10	7.95	8.05	7.11	5.96	
anthracene	1.86	1.88	1.31	2.17	1.50	1.53	
Total	50.32	40.23	33.36	29.39	26.61	25.89	

A-original oil

B-oil heated with hydrogen, no catalyst

C-oil heated with hydrogen and pyrite

D-oil heated with hydrogen and cobalt molybdate

E-oil heated with hydrogen and coal ash

F-oil heated with hydrogen and SRC solids

Three runs were made for each treatment with a relative standard deviation between runs of $\pm 8\%$ of the determined mean weight per cent.

Table VI. Effect of Iron Concentration on Hydrogen Consumption and Rate of Hydrodesulfurization of a Coal/Oil Slurry

solvent (LRD)/coal = 2, T = 410°C, 120 minutes, 1000 rpm

Wt. % Fe	Initial Pressure ($\times 10^{-3}$ psig)	Final Pressure ($\times 10^{-3}$ psig)	Partial Pressure (psig)					Sulfur Content of Liquid Products*	H ₂ /H ₀ **
			H ₂ (10^{-3})	H ₂ S	CO ₂	CH ₄	C ₂ -C ₅		
0.	2.28	1.71	1.21	35	49	167	114	0.374	0.57
0.	1.92	1.59	1.11	37	56	155	95	0.417	0.62
0.	2.09	1.70	1.25	36	44	135	90	0.350	0.64
0.	2.04	1.65	1.19	48	53	141	83	0.411	0.63
0.	2.01	1.54	--	--	--	--	--	0.402	--
1.0	2.21	1.70	1.19	5.9	54	200	114	0.374	0.37
2.0	1.52	1.23	0.773	0.0	42	172	102	0.318	0.35
2.0	1.66	1.34	0.851	0.0	64	189	112	0.373	0.56
4.0	1.98	1.41	0.923	0.0	50	189	107	0.360	0.35
4.0	1.48	1.22	0.863	0.0	24	120	73	0.329	0.50
7.7	2.10	1.62	1.15	0.0	49	172	107	0.294	0.28
7.7	2.04	1.55	1.11	0.0	46	152	98	0.273	0.59
13.3	2.01	1.46	1.02	0.0	45	157	99	0.237	0.55
13.3	1.99	1.44	1.01	0.0	45	156	92	0.271	0.25
13.3	2.00	1.48	1.08	0.0	42	136	87	0.24	0.58

*,** same as in Table II

Table VII. Product and Sulfur Distribution in Small Tubing-Bomb Reactor

solvent(tetralin)/coal = 2, T = 410°C, 30 minutes

runs	A**	B	C	D
catalyst (7.7%)	-	Fe	Co-Mo-Al	Co-Mo-Al
gas (Pi)	air (1atm)	air (1atm)	H ₂ (1360 psig)	H ₂ (1200 psig)
cycles per minute	100-500	100	100	~1000
product, %				
oil + gases	21.0	23.0	22.4	31.4
asphaltene	18.2	17.4	23.8	33.3
presphaltenes	45.8	43.4	31.4	24.8
insolubles	15.1	16.2	22.4	10.5
sulfur, %				
oil	0.14	0.13	0.06	-
asphaltene	1.76	1.41	1.39	-
presphaltenes	0.53	0.31	0.91	-
insolubles	4.29	3.66	3.38	-
total sulfur, grams				
reactants	0.080	0.081	0.065	-
products (except gases)	0.055	0.075	0.062	-
oil	0.009	0.009	0.003	-
benzene solubles	0.017	0.015	0.010	-
pyridine solubles	0.023	0.019	0.016	-
naphthalene/tetralin (GC peak ratio)	0.57	0.59	0.29	-

*: based on dmmf coal and solvent-free

**: average value of 4 runs at 100, 250, 350 and 500 cycles per minute.

Table VIII. Effect of Catalyst, Hydrogen Atmosphere, and Solvent-to-Coal Ratio on Rate of Hydrodesulfurization of a Coal/Oil Slurry

T = 410°C, 120 minutes, 1000 rpm

Weight Percent of Catalyst (Co-Mo-Al*)	Atmosphere	Solvent-to-Coal Ratio	Percent Sulfur Content of Liquid Fraction of Reaction Product **	Tetralin/Naphthalene Ratio***
None	2000 psig H ₂	3:1	0.42	0.190
None	2000 psig H ₂	3:1	0.42	
None	2000 psig N ₂	3:1	0.42	0.066
15.0	1000 psig N ₂	3:1	0.30	0.066
15.0	2000 psig H ₂	3:1	0.29	
15.0	2000 psig H ₂	3:1	0.17	-
15.0	2000 psig H ₂	3:1	0.17	
None	2000 psig H ₂	2:1	0.39(avg of 4 runs)	0.16
15.0	2000 psig H ₂	2:1	0.24	0.49
15.0	2000 psig H ₂	2:1	0.19	
15.0	1000 psig H ₂	2:1	0.36	-
15.0	1000 psig H ₂	2:1	0.38	

*,**,*** same as in Table II

Table IX. Effect of Reaction Time and Atmosphere on Conversion of Coal to Liquid

Atmosphere	Reaction Time	Cresol Solubles(%)	Cresol Soluble Yield (%)*
H ₂	2 hrs.	96.20	95.81
N ₂	2 hrs.	89.78	66.81
H ₂	15 min.	92.3	78.23
N ₂	15 min.	89.73	66.58

Reaction Conditions:

Temperature = 410°C
Solvent-to-Coal Ratio = 2:1
Non-Catalytic

*Cresol Soluble Yield = $\frac{C - A}{1 - M} \times 100$ where C = charge of moisture free coal; A = the recovered insoluble residue; M = the fraction of mineral matter in dry coal.

FLASH PYROLYSIS COAL TAR. W.G. Willson, S.A. Qader, E.W. Knell.
Occidental Research Corporation, 1855 Carrion Road, La Verne, Ca 91750.

A Wyoming subbituminous coal was subjected to flash pyrolysis in bench scale and PDU flow systems. A series of coal pyrolysis tests were conducted in a 1 lb/hr bench scale reactor to obtain tar yield and characterization data as functions of pyrolysis conditions. Temperatures employed varied from 1000-1400°F and residence times of 1.5 and 3.0 seconds were used. Tar yield was found to be quite sensitive to both variables. The properties of oils and asphaltenes were found to be insensitive to temperature but varied significantly with residence times under the test conditions. Tar produced in the PDU was found to be quite similar to that produced in the bench scale reactor under similar reaction conditions.

THE SRC II PROCESS

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I. INTRODUCTION

In the original P&M Solvent Refined Coal Process,¹ now designated SRC I, coal is dissolved under moderate hydrogen pressure in an internally generated heavy aromatic solvent to produce a liquid from which mineral matter is removed by filtration. Solvent is recovered for reuse by vacuum distillation; the distillation residue which is a solid under ambient conditions is a very low ash, low sulfur fuel known as Solvent Refined Coal. The current state of development of the SRC I process is indicated by the highly successful operation of two pilot plants; a 6 ton/day pilot plant at Wilsonville, Alabama,² which is currently sponsored by ERDA and EPRI and is operated by Catalytic, Inc., and a larger 50 ton/day pilot plant at Fort Lewis, Washington,³ which is sponsored by ERDA and is operated by The Pittsburg & Midway Coal Mining Co., a subsidiary of Gulf Oil Corp.

In an improved version of the process, designated SRC II,⁴ a portion of coal solution is recycled as solvent in the process in place of the distillate solvent of the original SRC I process. This improved process increases the conversion of dissolved coal to lower molecular weight fuels; the primary product of this process is a liquid fuel in place of the solid product of the SRC I process.

In the modified process, a fraction of the coal solution is used in feed slurry formulation; the remainder is available for product isolation (Figure 1). The fuel value could be recovered by filtration in which case the primary fuel product would be the filtrate, a heavy, sometimes viscous liquid product. Laboratory work has demonstrated, however, that under appropriate reaction conditions the conversion of high molecular weight dissolved coal to lower molecular weight products is adequate to allow recovery of the fuel product by distillation, thereby eliminating the difficult and expensive filtration step. The primary product is a low sulfur distillate fuel oil with a distillation range corresponding roughly to that of recycle solvent of the SRC I process. The residue from the vacuum distillation consists of three components: ash, insoluble organic matter, and material which has dissolved but is not distillable; i.e., similar to the solid SRC of the SRC I process. By appropriate selection of reaction conditions, the distillation residue yield can be reduced to that required for hydrogen generation for the process.

The increased conversion to light products in the SRC II process is caused by a combination of three factors:

1. Pressure and residence time used in the SRC II process are increased over those typically used in the SRC I process.
2. Recycle of the coal solution allows additional reaction time for conversion of high molecular weight dissolved coal to lower molecular weight products.
3. The concentration of mineral matter, which is known to function as a catalyst for SRC reactions, is increased.

In this paper, development of the SRC II process at the P&M Merriam Laboratory is described. In the first stage of development, this work defined in general terms conditions under which the SRC II process could be conducted and product yields and properties were determined. In later work, which was designed to provide information for SRC II operation at the Fort Lewis Pilot Plant, a systematic study was made to determine the effect of the following variables: coal concentration in the feed slurry, dissolver residence time, dissolver temperature, and hydrogen feed rate. Pressure effects were not a part of the latter study (the objective was to make the study at the minimum practical pressure) but some comparisons between runs at varying pressures are available.

II. EXPERIMENTAL

Materials: Coal used was a blend of Kentucky Nos. 9 and 14 from P&M's Colonial Mine in Hopkins County. Most of the work described in this paper was carried out with one lot, designated lot 5, but several runs (GU 120, GU 4A, GU 135R) carried out with another lot, lot 4, which was of higher iron content are also presented. Coal analyses are given in Table I. Recycle solvent was generally internally generated. When insufficient internally generated solvent was available for start up of a run, recycle solvent from the Fort Lewis Pilot Plant was used.

Equipment: A simplified schematic of the laboratory scale continuous reactor used in the present work is shown in Figure 2. The reaction subsystem consists of a preheater and one or two dissolvers operated in series. The preheater is a 4.5 ft section of 11/16 inch ID pressure tubing (316 stainless steel) and each of the dissolvers is a 7 ft section of the same diameter tubing. The preheater is typically operated with a temperature profile to allow a temperature of 400°C in the top zone. Due to the low temperature of this vessel, preheater volume is not included in calculation of reactor volume, residence times, or feed rates expressed in lb/hr/ft³. Reaction volume for each dissolver (corrected for thermowell volume) is 452 ml (0.01596 cu ft) which corresponds to 520 g of slurry to fill. Thus, a slurry feed rate of 1040 g/hr corresponds to a nominal liquid residence time of 1 hr with both dissolvers in use.

TABLE I
Feed Coal Analysis
(Dry Basis)

PROXIMATE ANALYSIS	Lot 4	Lot 5	ULTIMATE ANALYSIS	% Weight	
				Lot 4	Lot 5
% Ash	11.39	8.87	Carbon	69.54	71.89
% Volatile	38.12	38.12	Hydrogen	4.94	5.10
% Fixed Carbon	50.49	53.01	Nitrogen	1.22	1.24
	100.00	100.00	Chlorine	0.03	0.06
			Sulfur	4.11	3.21
			Ash	11.39	8.87
Btu/lb	12700	13238	Oxygen (diff)	8.77	9.63
				100.00	100.00
SULFUR FORMS			MINERAL ANALYSIS	% Weight	
				Ignited Basis Lot 4	Ignited Basis Lot 5
% Pyritic Sulfur	2.65	1.87	Phos. pentoxide, P_2O_5	0.37	0.14
% Sulfate Sulfur	0.54	0.27	Silica, SiO_2	31.56	39.10
% Organic Sulfur	0.92	1.07	Ferric oxide, Fe_2O_3	38.76	31.78
% Total Sulfur	4.11	3.21	Alumina, Al_2O_3	22.93	20.91
			Titania, TiO_2	0.98	0.98
Free Swelling Index	3.5	5	Lime, CaO	1.79	2.00
			Magnesia, MgO	0.45	0.65
			Sulfur trioxide, SO_3	1.27	1.71
			Potassium oxide, K_2O	1.34	2.20
			Sodium oxide, Na_2O	0.31	0.38
			Undetermined	0.24	0.15
				100.00	100.00

Reactor effluent passes from the dissolver to a pressure letdown and sample collection system. This system accomplishes the separation of gases, water, and light oil from the coal solution. The resultant stripped coal solution is collected for intervals of from 2 to 4 hrs; further workup of the coal solution (slurry preparation and product isolation) is performed manually in batch procedures.

Operating Procedures: A typical run in which a single condition is investigated typically requires on the order of 60-100 hours of continuous operation to reach steady state conditions followed by a period of steady state operation during which data for yield determinations and product properties are collected.

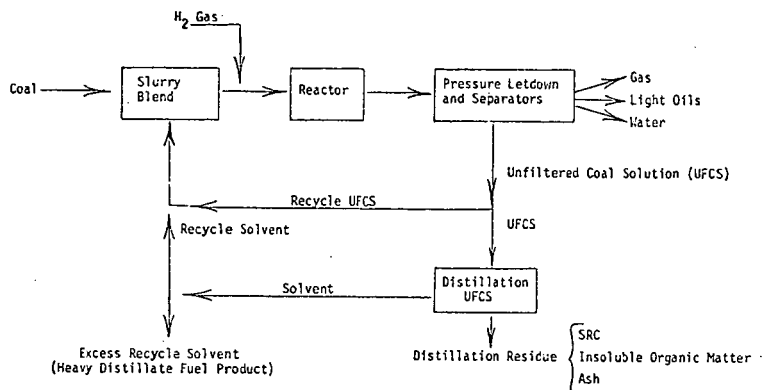
The most satisfactory method to reach steady state operation in the SRC II mode is to begin operation with a slurry of distillate solvent and coal. As coal solution is collected, the required amount is blended with coal and added to the reactor slurry feed vessel. This process is continued until a satisfactory period of steady state operation is achieved. The approach to lineout is followed by empirical run control measurements which have been discussed previously⁵ and will not be reiterated here. A typical run control chart is shown in Figure 3. For this run it can be seen that feed slurry ash increased as coal solution was recycled until a steady state concentration of about 9% was observed, blackness^a increased to a steady state value slightly below 20 and IR^a (except for the low value for the initial sample which is a reflection of the lower hydrogenation state for the startup solvent) showed some oscillation but no long term trends. These control measurements together with gas yields, distillation results, etc. give rapid indications of the progress of the run and indicate when steady state operation is achieved; steady state operation is later confirmed by constancy of product yields and compositions.

A portion of the coal solution is used in slurry formulation; the remainder is available for product isolation. Yields presented in this paper are for the process involving distillation of unfiltered coal solution to produce a distillate fuel product and a distillation residue. Yields of the three components of the distillation residue--ash, insoluble organic matter, and solid SRC (dissolved but not distillable)--will be reported separately. In the actual laboratory workup a filtration step may precede the distillation. In either case the distillation is a batch operation carried out in laboratory equipment with an oil vacuum pump. Typically, pressure early in the distillation is below 1 mm Hg and increases as the distillation temperature exceeds 250°C. Distillations are terminated before serious decomposition takes place; the normal distillation endpoint is about 270°C head temperature at which time the distillation pressure has often increased to about 3-5 mm Hg.

In the GU 137R-GU 160R series, solids level in the feed slurry was not allowed to exceed 48%. (Solids include ash and insoluble organic matter in the unfiltered coal solution used in slurry formulation as well as the added coal). This constraint was imposed by consideration of possible operational constraints for the Fort Lewis Pilot Plant. At the higher coal concentrations used, this limitation necessitates the use of some recycle solvent in slurry formulation. This is illustrated in the simplified flow diagram shown on the following page where solids level in the feed slurry can be controlled at a constant coal concentration by varying the relative amounts of unfiltered coal solution and recycle solvent used in slurry preparation. At a coal

^aBlackness is a measure of absorbance of the coal solution in the visible region. IR, determined from the infrared spectrum of the coal solution, is a measure of the hydrogenation state of the coal solution and increases as the degree of hydrogenation of the coal solution increases. See reference 5 for a complete description of these measurements.

concentration of 30%, no recycle solvent is required. At a coal concentration of 40%, other components of the feed slurry were 51% unfiltered coal solution and 9% recycle solvent, and at a coal concentration of 45% other components of the feed slurry were 27.5% unfiltered coal solution and 27.5% recycle solvent. As currently practiced, the recycle solvent used in a slurry formulation is the same material as the distillate fuel product of the SRC II process. Unfiltered coal solution is distilled; the required amount of distillate is used in slurry formulation and the remainder is available as product.



Conditions Explored: Factors and levels which were investigated in the GU 137R-GU 160R series are as follows:

Factor	Levels
Coal concentration in feed slurry, %	30, 40, 45
Dissolver Temperature, °C	445, 455, 465
Residence Time, hr	2/3, 1, 1 1/2
Hydrogen Feed Rate, wt % based on feed slurry	4.9, 6.3

A complete factorial would require an excessive number of runs, so only selected conditions were investigated. Pressure which is known to be an important variable was not investigated as the objective was to make the current study at the minimum practical pressure. Several runs outside of this series (made at other conditions including other pressures) are included in this paper for comparison purposes.

Variables examined were not varied over a wide range; previous work had defined in general terms conditions over which the SRC II process was operable. For example, at temperatures below about 445°C, the rate for

conversion of asphaltene to oil is too low to sustain satisfactory operation without an excessively long residence time and at temperatures much in excess of 465°C, coking becomes a problem.

It was generally possible to attain satisfactory steady state operation and obtain reliable yield data for the 1 hour and 1.5 hour residence time runs but experimental difficulties were often experienced with shorter residence times. The primary problem experienced in the shorter residence time runs was with feed slurry viscosity. At the shorter residence time, conversion of SRC to oil is lower and feed slurry viscosities are higher. Under such conditions, feed slurry viscosity would lead to slurry pump failure which would force run termination before a satisfactory period of steady state operation was achieved.

Yield Reporting: Yields are reported on a loss free, forced ash balance basis. Actual material accountability was excellent with reactor output normally varying from input by only a few tenths of a percent. Yields considered in this paper are hydrocarbon gas yields (C₁-C₄), oil yields, SRC yields, and, in one comparison, insoluble organic matter (IOM) yields. Methane through butane yields are considered rather than total gas yields or total hydrocarbon gas yields as C₁-C₄ yields are not subject to variability in operation of the reactor sampling system as are total gas yields or total hydrocarbon gas yields. (The latter yields are subject to variable efficiency of removal of heavier hydrocarbon gases from the product gas stream.)

Total oil yields are considered rather than yields of discrete distillation fractions; this eliminates any problems which might be introduced by any variability in the fractionation procedure.

Total oil yields include the heavy distillate fuel cut (>249°C, equivalent to recycle solvent) and the cuts which correspond to the wash solvent (193-249°C) and light oil (<193°C) cuts of the SRC I process. The fraction noted as "unidentified gas"^a has been shown to consist primarily of C₅-C₈ hydrocarbons so this category is included with the total oil yield.

Distillation residue produced from distillation of unfiltered coal solutions contains ash, insoluble organic matter, and SRC. As ash is independent of processing conditions and the insoluble organic matter yield varies over only a small range, distillation residue and SRC yields respond to changes in operating conditions in a parallel manner. In this treatment, SRC yields rather than total distillation residue yields are considered. Insoluble organic matter yields are also considered where they are of interest.

Water yields appear anomalously high in some cases. The high water yields may be related to hygroscopic properties of the slurry or, more likely, may be due to oxidation of hot feed slurry. Forced carbon

^a Difference between total weight of reactor output gas and weight of identified gases.

balance yields have been calculated⁷ to correct for the high water yields but are not used in this paper. Reported water yields are for the crude aqueous phase; the aqueous phase typically is about 92% water containing dissolved ammonia, hydrogen sulfide, carbonate and phenol.

Hydrogen consumptions are calculated by two methods. In the hydrogen gas balance method, consumption is determined by subtracting the amount of hydrogen in the output gas from the calibrated hydrogen gas input. This method involves the determination of a small difference between two large numbers, both of which are subject to a high experimental uncertainty. As this method is generally considered unsatisfactory due to the large experimental uncertainty, hydrogen consumptions are also calculated by an alternate method.

A somewhat improved estimation of hydrogen consumption is obtained by product analysis. The amount of hydrogen in the products is determined from the product distribution (forced carbon balance basis) and the composition (% hydrogen) of each product. Hydrogen consumption is then equal to the amount of hydrogen in the products less the hydrogen content of the feed coal.

III. RESULTS

SRC I - SRC II Comparison: SRC I runs are generally made at shorter residence times and lower pressures than are SRC II runs. In normal operation, conditions for SRC I runs are selected to obtain a breakeven yield of recycle solvent but with no attempt to significantly increase the solvent yield beyond that required for recycle. Three laboratory runs are compared in Table II. These runs represent an SRC I run made under typical SRC conditions; an SRC I run made under conditions typical of SRC II operations, and a typical SRC II run. These runs were made with lot 4 coal. (All other runs discussed in this paper were made with lot 5 coal.) Under the typical SRC I conditions, a breakeven yield of recycle solvent is obtained but there is no excess heavy oil while the primary product of the process is the solid SRC which is obtained in 56% yield. In the SRC I run made under the conditions typical of the SRC II process, a 16% yield of excess recycle solvent is obtained (total distillate oil yield of 29%) and the SRC yield is decreased to 35%. Under the same conditions but in the SRC II mode of operation the SRC yield is decreased to only 16% and the total distillate oil yield is increased to 44%. The improved conversion of solid SRC to lighter products in the SRC II runs is due to a combination of the increased mineral matter (catalyst) concentration and the recycling of the coal solution which allows additional reaction time for conversion of solid SRC to distillate products.

The results of this SRC II run indicate that the concept of the SRC II operation with recovery of the fuel product by distillation is practical and that the yield of distillation residue can be reduced to that required for hydrogen generation for the process. It also indicates that the activity of the naturally occurring catalyst in the coal is adequate to accomplish the required conversion. That the use of a

separate catalyst is not required is a major advantage of the SRC II process. As the conversion to low molecular weight products is adequate to allow isolation of the fuel product by distillation, the difficult and expensive solids removal step as well as mineral residue drying and product solidification steps may be eliminated which greatly simplifies the process. Due to the elimination of filters, dryers, and solidification equipment, it has been estimated that the cost of the SRC II product should be no more than that of the solid SRC I product.⁴

Pressure: As noted previously, pressure was not among the variables included in the current study. It is generally recognized that as pressure is increased, desired hydrogenation rates are increased and operability is improved. The objective of this study was to study other variables at the minimum practical pressure. Work at pressures lower than the 1900 psig of this study had shown that it was possible to sustain SRC II operation at a lower pressure but only with significant increases in residence time. It was found to be impossible (in laboratory equipment) to maintain operation at 1500 psig with other conditions similar to those of GU 135R (Table II). In order to keep the viscosity of the feed slurry manageable, residence time was gradually increased. It was eventually found to be possible to maintain satisfactory operation but only after the residence time was increased to 1.7 hr. These conditions resulted in a high conversion of SRC to lighter products (SRC yield of only 13%) but only with an excessively high gas yield, (C₁-C₄ yield of 24.4%, twice that reported for GU 135R).

In view of unsatisfactory results at pressures significantly below 1900 psig and the desire to operate at the minimum practical pressure, all further work was carried out at 1900 psig (with the exception of GU 160A and GU 160B which carried out pressures of 2000 and 1800 psig, respectively).

Coal Concentration: The effect of coal concentration is readily apparent from Table III. These runs were all made with a dissolver temperature of 455°C, a pressure of 1900 psig, and a residence time of one hour. No correlation between hydrocarbon gas yields and coal concentration is apparent, but there are near linear relationships between coal concentration and yields of SRC and oil. Oil yield decreases with increasing coal concentration while SRC yield increases with increasing coal concentration.

Residence Time: Three levels of residence time were investigated. Most runs were made with a nominal one hour liquid residence time with a limited number of runs made with a 1.5 or 2/3 hour residence time. The 2/3 hour residence time runs were made only with low coal concentrations and were generally subject to operating difficulties. Results in Table IV show that the reduction in residence time from one hour to 2/3 hour results in a significant increase in SRC yield and a smaller

TABLE II
Comparison SRC I and SRC II Runs

	Typical SRC I Run (GU 120)	SRC I Under Typical SRC II Conditions (GU 4A)	SRC II (GU 135R)
Reaction Conditions			
Pressure, psig	1425	2000	2000
Dissolver Temperature, °C	450-455	455-465	465
Nominal Residence Time, hr	0.4	1.0	1.0
Hydrogen Feed, wt % of slurry	2.1	5.3	4.9
Feed Slurry Composition			
% Coal	39.0	35.0	35.0
% Coal Solution	--	--	65.0
% Distillate Solvent	61.0	65.0	
Yields, Wt % Based on Coal			
C ₁ -C ₄	2.9	12.5	12.2
CO, CO ₂ , H ₂ S	3.0	3.6	3.5
Water	6.4	7.6	11.4
Light Oil, C ₅ -249°C	16.4	13.6	19.5
Heavy Distillate, <249°C	--	15.7	24.8
Total Oil	16.4	29.3	44.3
SRC	56.3	34.8	15.9
IOM	5.3	4.4	4.5
Ash	11.3	11.3	11.5
H ₂ Reacted (gas balance)	1.6	3.5	4.0

TABLE III
Effect of Coal Concentration in Feed Slurry

Run No.	% Coal	C ₁ -C ₄ Yield	Oil Yield	SRC Yield
GU 137R	30	10.9	37.4	23.2
GU 152R	30	10.7	39.9	24.2
GU 138R	40	10.0	29.5	34.1
GU 154R	40	9.6	30.5	35.0
GU 139R	45	11.6	24.5	41.3
GU 147R	45	(11.6) ^a	25.6	40.0
GU 153R	45	8.2 ^b	25.4	41.6

a) Estimated

b) Reported value is suspect

but still significant decrease in oil yield. It is suspected that the increased gas yield reported for the 2/3 hour run (GU 142R) is erroneous. This suspicion is confirmed by another run made under the same conditions except for an increased hydrogen feed rate (GU 151R). The latter run is excluded from the following comparison as the run was terminated before satisfactory steady state operation was achieved. (A run which approaches and does not reach steady state operation may produce satisfactory gas yield data although reliable oil and SRC yields are not available.)

An increase in residence time from 1 to 1 1/2 hour resulted in increases in gas and oil yields and the expected decrease in SRC yield.

TABLE IV
Effect of Residence Time

A. 30% Coal Concentration

Run No.	Residence Time, Hr	C ₁ -C ₄ Yield	Oil Yield	SRC Yield
GU 142R	0.69	12.9 ^a	34.7	30.4
GU 137R	0.97	10.9	37.4	23.2
GU 152R	1.00	10.7	39.9	24.2

B. 40% Coal Concentration

Run No.	Residence Time, Hr	C ₁ -C ₄ Yield	Oil Yield	SRC Yield
GU 138R	1.01	10.0	29.5	34.1
GU 154R	1.00	9.6	30.5	35.0
GU 141R	1.59	13.9	35.4	26.8

C. 45% Coal Concentration

Run No.	Residence Time, Hr	C ₁ -C ₄ Yield	Oil Yield	SRC Yield
GU 139R	1.02	11.6	24.5	41.3
GU 158R	1.48	14.3	33.0	27.9

All runs at 455°C

^aReported value is suspect

Temperature: The effect of temperature is shown in Table V. Most runs were made at a dissolver temperature of 455°C with a limited number of runs at temperatures of 445 or 465°C. Although the magnitude of the effect of temperature change is quite variable, it is seen that, over the range investigated, increasing temperature generally results in increases in gas and oil yields and decreases in SRC yield. At a 30% coal concentration and one hour residence time, increasing the temperature from 445 to 455°C results in a significant decrease in SRC yield and increase in oil yield while an increase from 455 to 465°C (1 hour residence time, 40% coal) results in only a small (probably insignificant) decrease in SRC yield and increase in oil yield.

The temperature effect noted in the 2/3 hour runs is of particular interest. Oil and SRC yields for the higher temperature (465°C) runs appear more favorable (although the magnitude of the improvement is questionable due to the usual mechanical problems experienced with 2/3 hour runs), but the increase in insoluble organic matter (IOM) yield is regarded as being of particular significance. This substantial increase in IOM yield is believed to be an indication of generally unsatisfactory operating conditions; conditions may be near those which will result in coke formation, catalyst destruction, and reactor plugging.

TABLE V
Effect of Temperature

A. 30% Coal 2/3 Hr

Run No.	Temp, °C	C ₁ -C ₄ Yield	Oil Yield	SRC Yield	IOM Yield
GU 142R	455	12.9	34.7	30.4	4.8
GU 150R	465	15.3	39.0	17.2	7.8
GU 160RA ^a	465	16.9	38.0	20.9	6.3
GU 160RB ^a	465	(16.9) ^b	37.3	21.5	7.1

B. 30% Coal 1 Hr

Run No.	Temp, °C	C ₁ -C ₄ Yield	Oil Yield	SRC Yield	IOM Yield
GU 155R	445	10.0	35.1	31.1	4.3
GU 137R	455	10.9	37.4	23.3	4.3
GU 152R	455	10.7	39.9	24.2	4.9

^aGU 160RA was made at a pressure of 2000 psig and GU 160RB was made at a pressure of 1800 psig. All other runs were made at the normal 1900 psig.

^bEstimated.

C. 40% Coal 1 Hr

Run No.	Temp, °C	C ₁ -C ₄ Yield	Oil Yield	SRC Yield	10M Yield
GU 138R	455	10.0	29.5	34.1	5.4
GU 146R	465	11.7	28.7	33.7	6.7

The normal hydrogen feed rate was about 4.9 wt % based on feed slurry. In several runs a hydrogen feed rate increased by about 30% (6.4 wt % based on feed slurry) was used. Results for three of the increased hydrogen feed rate runs are compared with the appropriate control runs in Table VI. Any improved reaction due to increased hydrogen feed rate is apparently nullified by the reduction in liquid residence time caused by the increased gas volume. At the levels studied, hydrogen feed rate appears to have no significant effect on product yields. This conclusion should not be considered necessarily valid for larger reactors because of anomalous bubble behavior in the small diameter reactor used in this work.

TABLE VI
Effect of Hydrogen Feed Rate

Run No.	% Coal	Residence Time	H ₂ Feed		C ₁ -C ₄ Yield	Oil Yield	SRC Yield
			Wt % Based on Slurry	MSCF Ton of Coal			
GU 137R	30	0.97	4.63	58.1	10.9	37.4	23.2
GU 152R	30	1.00	6.28	78.9	10.7	39.9	24.2
GU 138R	40	1.01	4.63	43.6	10.0	29.5	34.1
GU 154R	40	1.00	6.23	58.6	9.6	30.5	35.0
GU 139R	45	1.04	4.83	40.4	11.6	24.5	41.3
GU 153R	45	0.99	6.06	50.7	8.2 ^a	25.4	41.6

All runs at 455°C

^aValue suspect.

Hydrogen Consumption: Hydrogen consumptions generally vary in a manner consistent with the varying conditions. Precise correlations are difficult, however, in view of the relatively high experimental error in the hydrogen consumption determination. A discussion of this topic is beyond the scope of this paper. Hydrogen consumptions of the run in this report range from under 3% to 4.6%. In a typical run in which a satisfactory conversion of SRC to lighter products is achieved, hydrogen conversion is generally 4.0 to 4.5 wt % based on the feed coal.

Product Properties: Product properties have generally been observed to vary in a rational manner with operating conditions, but a detailed discussion of this topic is beyond the scope of this paper. However, properties have varied over only a relatively narrow range. The following ranges of elemental composition and specific gravity for the heavy distillate fuel product (>249°C) have been observed in the GU 136R-GU 160R series.

Carbon	86.8	-	88.1
Hydrogen	7.6	-	8.5
Sulfur	0.22	-	0.35
Nitrogen	1.1	-	1.4
Oxygen	2.5	-	3.6
Specific Gravity	1.027	-	1.052

IV. CONCLUSIONS

It has been possible to sustain satisfactory SRC II operation at a pressure of 1900 psig and residence times of about 2/3 to 1 1/2 hours and temperatures of 445 to 465°C. Under the better conditions, distillation residue yield does not exceed that required for hydrogen generation for the process. Increasing coal concentration in the feed slurry results in increasing the yield of vacuum residue. Increasing temperature results in decreased vacuum residue yield and increased yield of light products but 465°C appears to be approaching the maximum operable temperature. Over the range investigated, hydrogen addition rate does not appear to be a significant variable in the laboratory apparatus. Increased residence time results in decreased yields of vacuum residue and increased yields of light products.

An interesting observation on this series of runs is the apparent near invariance of distillate oil yield with coal feed rate when both are expressed in terms of productivity per unit of reactor volume per hour.⁶ This is illustrated in Figure 4.

Properties of the distillate fuel products vary in a predictable manner but compositions vary over a limited range. In all cases, the distillate fuel readily surpasses EPA standards for SO₂ emission and also meets many of the more stringent requirements for major metropolitan areas.

Hydrogen consumption measurements are subject to a relatively high experimental error but generally vary in a manner consistent with condition variations and fall in the range of 4.0-4.5% for runs with satisfactory conversion of SRC to lighter products.

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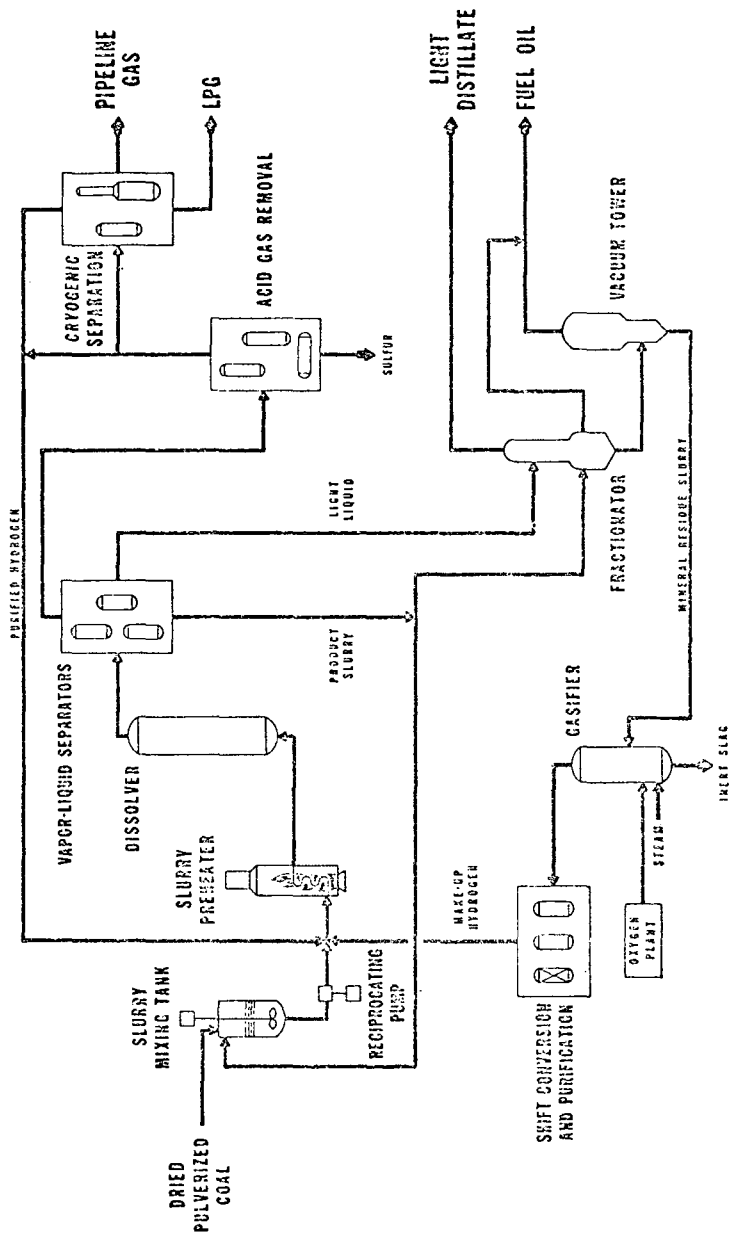
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FIGURE 1

THE SRC III PROCESS



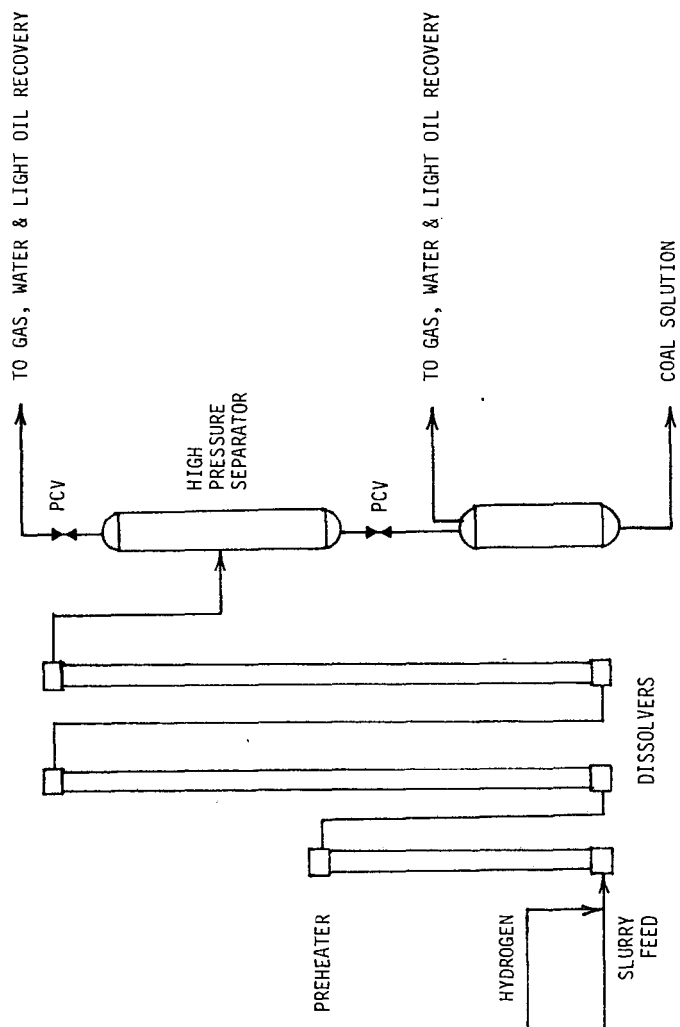


FIGURE 2 GU 5 REACTOR

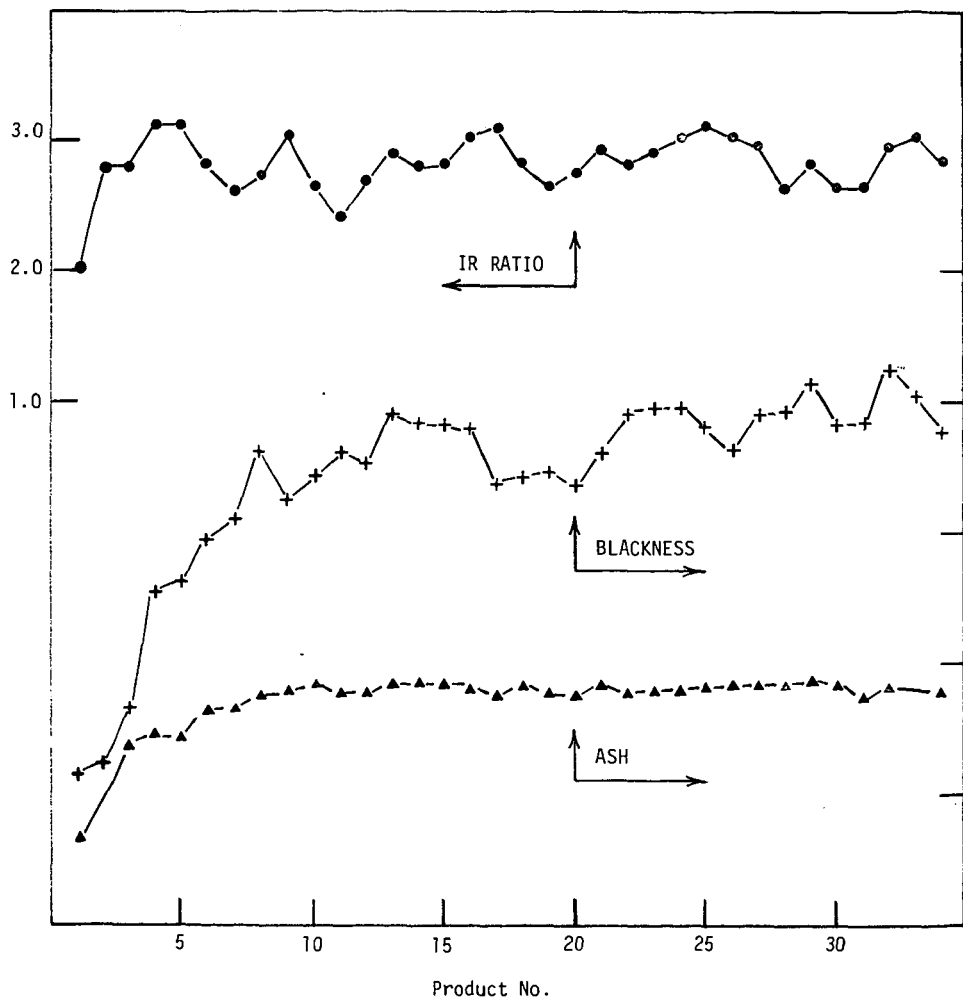
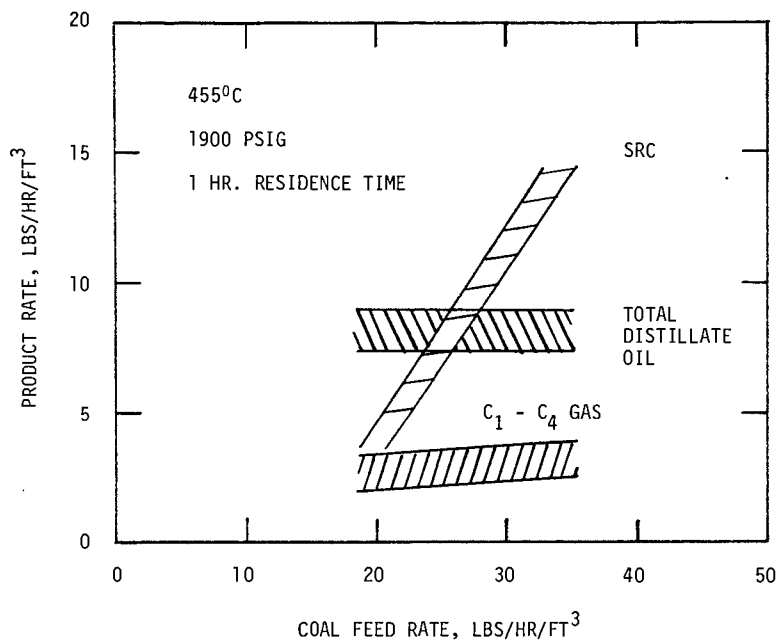


FIGURE 3 GU 146R RUN CONTROL DATA

Figure 4
PRODUCTION RATES VS COAL FEED RATE



A Dispersion Model for the Solvent Refined Coal Process

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In the SRC process, pulverized coal is mixed with an internally generated coal-derived solvent. The resulting slurry and hydrogen gas are pumped and preheated to 780-850°F through a gas-fired preheater connected to a dissolver section for further reaction. The coal is depolymerized by thermal cracking and reacts with hydrogen to produce lower molecular weight materials. At the same time some of the sulfur contained in the coal reacts with hydrogen to produce gaseous H_2S which is then removed by standard technology.

In this paper an axial dispersion model for two-phase flow is applied to study the kinetics of hydrogenation, desulfurization, and coal conversion in the SRC process. In applying the model, the Peclet number for the preheater section is assumed to be infinite, while the Peclet number for the dissolver will usually be around unity. Physically this means that the dissolver will experience a significant amount of axial dispersion. In applying the dispersion model to the SRC process, one needs to know reaction kinetics rate expressions for the pertinent reactions. Considerable research has been conducted concerning the kinetics of coal solvation and sulfur removal. Wen and Han (1975) have determined rate constants using coal liquefaction and desulfurization data gathered primarily from studies by Pittsburgh and Midway Coal Mining Co., the University of Utah, and the Colorado School of Mines. These researchers were able to fit data from the above sources with an empirical expression for the rate of coal dissolution; however, no kinetic expression was obtained for desulfurization and the effect of hydrogen partial pressure on coal dissolution and sulfur removal was not firmly established. It is likely that the different types of reactors and experimental procedures employed in the three laboratories made the data correlation more difficult. Very recently rate expressions describing the hydrogen transfer during the coal dissolution and hydrodesulfurization were determined by Pitts (1976). By performing batch autoclave experiments with Kentucky No. 9/14 coal, hydrogen gas, and creosote oil as solvent, he was able to develop kinetic models for rates of hydrogen consumption, coal dissolution and hydrodesulfurization. His results can be summarized as follows:

A. For hydrogenation: (Guin, et al., 1976)

$$r_{H_2} = -k_{H_2L} e^{-\Delta H/RT} c_{H_2L} \quad (1)$$

where $k_{H_2L} = 1.06 \times 10^5/\text{minute}$ and $\Delta H = 21 \text{ Kcal/mole}$

B. For hydrodesulfurization: (Guin, et al., 1977)

Two parallel independent first order reactions indicative of two different classes of more specific compounds were proposed to represent hydrodesulfurization kinetics, they are:

$$r_{s1} = -k_{s1}L c_{s1}L \quad (2)$$

$$r_{s2} = -k_{s2}L c_{s2}L \quad (3)$$

$$\text{where } k_{s1}L = 5.939 \times 10^{11} e^{-40.78 \text{ Kcal/RT}}$$

$$k_{s2}L = 1.664 \times 10^3 e^{-18.99 \text{ Kcal/RT}}$$

and the initial concentration of two sulfur species are

$$c_{s1}^0 = 1.53 \times 10^{-3} \text{ grams organic sulfur/cm}^3$$

$$c_{s2}^0 = 6.51 \times 10^{-3} \text{ grams organic sulfur/cm}^3$$

C. For coal dissolution:

Coal liquefaction was described by a model incorporating dissolved molecular hydrogen. The model assumed there are two differently reactive fractions of coal present in the reaction mixture. The rate equations were formulated to give two independent reactions, they are:

$$r_{c1} = -k_{c1}L c_{c1}L c_{H2L}^2 \quad (4)$$

$$r_{c2} = -k_{c2}L c_{c2}L c_{H2L}^2 \quad (5)$$

with initial ration of the reactive coal species given by $\frac{c_{c1}^0}{c_{c2}^0} = 0.771$ and

$$k_{c1}L = 3.269 \times 10^6 e^{-4.01 \text{ Kcal/RT}} \quad (6)$$

$$k_{c2}L = 6.988 \times 10^{10} e^{-21.4 \text{ Kcal/RT}} \quad (7)$$

with these available rate expressions, one can now formulate the design equations for the SRC reactor. These equations will be presented below.

For the preheater section:

$$\frac{dC_{H2g}}{dX} + \frac{k_{CaL}^I}{\hat{v}_g^I L} (C_{H2g} - C_{H2L}) = 0 \quad (8)$$

$$\frac{dC_{H2L}}{dX} - \frac{k_{CaL}^I}{\hat{v}_L^I} (C_{H2g} - C_{H2L}) + \frac{k_{H2L}^I L (1-f_g^I)}{\hat{v}_L^I} C_{H2L} = 0 \quad (9)$$

$$\frac{dC_{c1L}}{dX} + \frac{k_{c1L}^I L (1-f_g^I)}{\hat{v}_L^I} \left(\frac{C_r}{H}\right)^2 C_{c1L} C_{H2L}^2 = 0 \quad (10)$$

$$\frac{dC_{c2L}}{dX} + \frac{k_{c2L}^I L (1-f_g^I)}{\hat{v}_L^I} \left(\frac{C_r}{H}\right)^2 C_{c2L} C_{H2L}^2 = 0 \quad (11)$$

$$\frac{dC_{s1L}}{dX} + \frac{L (1-f_g^I)}{\hat{v}_L^I} k_{s1}^I C_{s1L} = 0 \quad (12)$$

$$\frac{dC_{s2L}}{dX} + \frac{L(1-f_g^I)}{\hat{v}_L^I} k_{s2L}^I C_{s2L} = 0 \quad (13)$$

with the conditions at $X = 0$:

$$\begin{aligned} C_{H_2g} &= C_{H_2g}^0 & C_{c1L} &= C_{c1L}^0 & C_{s1L} &= C_{s1L}^0 \\ C_{H_2L} &= C_{H_2L}^0 & C_{c2L} &= C_{c2L}^0 & C_{s2L} &= C_{s2L}^0 \end{aligned} \quad (14 \text{ a-f})$$

For the Dissolver section:

$$\frac{1-X_1}{Pe_g} \frac{d^2 C_{H_2g}}{dX^2} = \frac{dC_{H_2g}}{dX} + \frac{k_c^{II} a_L}{\hat{v}_g^{II} H} (C_{H_2g} - C_{H_2L}) \quad (15)$$

$$\frac{1-X_1}{Pe_L} \frac{d^2 C_{H_2L}}{dX^2} = \frac{dC_{H_2L}}{dX} - \frac{k_c^{II} a_L}{\hat{v}_L^{II} H} (C_{H_2g} - C_{H_2L}) + \quad (16)$$

$$\frac{k_{H2L} L (1-f_g^{II})}{\hat{v}_L^{II}} C_{H_2L}$$

$$\frac{1-X_1}{Pe_L} \frac{d^2 C_{c1L}}{dX^2} = \frac{dC_{c1L}}{dX} + \frac{k_{c1L}^{II} L (1-f_g^{II})}{\hat{v}_L^{II} H} (C_r)^2 x \quad (17)$$

$$C_{c1L} C_{H_2L}^2$$

$$\frac{1-X_1}{Pe_L} \frac{d^2 C_{c2L}}{dX^2} = \frac{dC_{c2L}}{dX} + \frac{k_{c2L}^{II} L (1-f_g^{II})}{\hat{v}_L^{II} H} (C_r)^2 x \quad (18)$$

$$C_{c2L} C_{H_2L}^2$$

$$\frac{1-X_1}{Pe_L} \frac{d^2 C_{s1L}}{dX^2} = \frac{dC_{s1L}}{dX} + \frac{L(1-f_g^{II})}{\hat{v}_L^{II} H} k_{s1L}^{II} C_{s1L} \quad (19)$$

$$\frac{1-X_1}{Pe_L} \frac{d^2 C_{s2L}}{dX^2} = \frac{dC_{s2L}}{dX} + \frac{L(1-f_g^{II})}{\hat{v}_L^{II} H} k_{s2L}^{II} C_{s2L} \quad (20)$$

with the conditions at $X = X_1$:

$$C_{H_2g}(X_1^-) = C_{H_2g}(X_1^+) - \frac{1-X_1}{Pe,g} \frac{dC_{H_2g}(X_1^+)}{dX} \quad (21)$$

$$C_{H_2L}(X_1^-) = C_{H_2L}(X_1^+) - \frac{1-X_1}{Pe,L} \frac{dC_{H_2L}(X_1^+)}{dX} \quad (22)$$

$$C_{C_1L}(X_1^-) = C_{C_1L}(X_1^+) - \frac{1-X_1}{Pe,L} \frac{dC_{C_1L}(X_1^+)}{dX} \quad (23)$$

$$C_{C_2L}(X_1^-) = C_{C_2L}(X_1^+) - \frac{1-X_1}{Pe,L} \frac{dC_{C_2L}(X_1^+)}{dX} \quad (24)$$

$$C_{S_1L}(X_1^-) = C_{S_1L}(X_1^+) - \frac{1-X_1}{Pe,L} \frac{dC_{S_1L}(X_1^+)}{dX} \quad (25)$$

$$C_{S_2L}(X_1^-) = C_{S_2L}(X_1^+) - \frac{1-X_1}{Pe,L} \frac{dC_{S_2L}(X_1^+)}{dX} \quad (26)$$

and the conditions at $X = 1$,

$$\frac{dC_{H_2g}}{dX} = 0 \quad \frac{dC_{H_2L}}{dX} = 0 \quad (27 \text{ a,b})$$

$$\frac{dC_{C_1L}}{dX} = 0 \quad \frac{dC_{C_2L}}{dX} = 0 \quad (28 \text{ a,b})$$

$$\frac{dC_{S_1L}}{dX} = 0 \quad \frac{dC_{S_2L}}{dX} = 0 \quad (29 \text{ a,b})$$

where X_1^- designates the position just inside the exit of the preheater and X_1^+ is the position just inside the inlet of dissolver.

Numerical Solution Technique

The set of first order ordinary differential design equations (8)-(13) for the preheater and transfer line section of SRC reactor can be integrated numerically from $X = 0$ to $X = X_1$ using a Runge-Kutta 4th order method. Once these equations are solved, we then proceed to solve the set of second order differential design equations (15)-(20) for the dissolver section of the SRC reactor. Equations (15)-(20) can also be integrated from $X = X_1$ to $X = 1$ using a 4th order Runge-Kutta procedure. In performing the integration, these second order differential equations have to be transformed into a system of first order differential equations. In order to integrate the system of first order differential equations from $X = X_1$ to $X = 1$, it is necessary to specify as many additional boundary conditions at $X = X_1$ as there are conditions to be satisfied at $X = 1$, we need six additional conditions at $X = X_1$, namely $C_{H_2g}(X_1^+)$, $C_{H_2L}(X_1^+)$, $C_{C_1L}(X_1^+)$, $C_{C_2L}(X_1^+)$, $C_{S_1L}(X_1^+)$, and $C_{S_2L}(X_1^+)$.

These values have to be guessed initially and successively adjusted to satisfy boundary conditions at $X = 1$. The Newton-Raphson method is used to make this adjustment.

In some cases when some of the parameters appearing in the governing differential equations (8-13) and (15-20) become very large, these differential equations may suffer from a difficulty known as stiffness when numerical solution of the equations is attempted. In such cases, the classical fourth order Runge-Kutta integration technique may fail to integrate the system of stiff equations due to numerical instability. However, it has been found that Gear's method (1971 a,b) is very powerful for solving stiff differential equations, and therefore, its use is recommended when the fourth order Runge-Kutta integration technique fails.

Results and Conclusions

In this section, data from the Wilsonville SRC pilot plant will be compared with results predicted using the model proposed in this paper. The operating conditions and reactor configuration at Wilsonville will be employed in the calculation of the extent of coal dissolution, hydrodesulfurization and hydrogen consumption based on the present proposed model.

The following operating conditions and reactor configuration were used in the simulation:

Coal Type	Kentucky 9/14 mixture
Hydrogen Pressure	1700 psig
Dissolver Temperature	820° F
Slurry Concentration	25%
Coal Feed Rate	500 lb./hr.
Gas Feed Rate	11.7 scf/lb. of coal
Hydrogen Concentration	85%
Dissolver Diameter	12 in.
Preheater Diameter	1½ in.
Transfer line Diameter	1½ in.
Preheater Volume*	1.6 ft. ³
Transfer line Volume	1.5 ft. ³
Dissolver Volume	18.0 ft. ³
Mean Reaction Temperature of Preheater and Transfer line	700° F

* The actual coal conversion reaction is initiated in the preheater coil. The temperature in this coil increases from 100° F to 800° F. Since the rate of conversion below 600° F is expected to be low, the reaction volume for the preheater was arbitrarily defined as the volume of that portion of the coil in which the temperature exceeds 600° F.

Based on the above conditions the following data can be obtained from literature correlating equations, which were needed in order to solve the design equations:

Preheater/Transfer Line		Dissolver	
\hat{V}_L	21.3 cm/sec	\hat{V}_L	0.335 cm/sec
\hat{V}_g	102.7 cm/sec	\hat{V}_g	1.80 cm/sec
Z_1	253 ft.	Z_2	23 ft.
$N_{Pe,L}$	1.18×10^3	$N_{Pe,L}$	0.97
$N_{Pe,g}$	4.83×10^2	$N_{Pe,g}$	4.66
f_g	0.44	f_g	0.06
k_{ca}	$3.57 \times 10^{-1}/\text{sec}$	k_{ca}	$5.53 \times 10^{-2}/\text{sec}$

<u>Preheater/Transfer Line (cont.)</u>			<u>Dissolver (cont.)</u>		
Henry's			Henry's		
Constant	2.8	g/cc of H_2 in vapor	Constant	2.5	g/c.c of H_2 in vapor
at 700°F		g/cc of H_2 in liquid	at 820°F		g/c.c of H_2 in liquid

Several cases were studied in this paper, and the parameters chosen for these are listed in Table 1.

Case A: simulates the Wilsonville SRC pilot plant. The yield of coal dissolution predicted by the present proposed model is 92% which is in good agreement with that measured under similar conditions in the Wilsonville pilot plant. The actual yield in the pilot plant was also around 92%.

Cases B & C: investigate the effect of mass transfer on the SRC process. In these two cases the mass transfer coefficients were chosen as 1/10 and 1/50 of that of Case A. The coal dissolution is reduced from 92% for Case A to 90.7% for Case B and to 85.5% for Case C. The reason for this is obvious because for the lower mass transfer coefficient, k_{ca} , the dissolved hydrogen concentration in the solvent will also be lowered. Since the coal dissolution rate depends on the second power of the dissolved hydrogen concentration as can be seen from eqs. (4) and (5), the reduction in coal dissolution is expected. However, the reduction of the hydrogen mass transfer coefficient does not effect the extent of hydrodesulfurization, because the desulfurization rate does not depend on the dissolved hydrogen concentration (eqs. 2 and 3).

Cases D & E: investigate the effect of Peclet number in the dissolver section on the yield of coal dissolution, hydrodesulfurization and hydrogen consumption. For a given reactor and given operating conditions, there will be a corresponding Peclet number. The higher the value of the Peclet number, the closer a plug flow condition will be approached; the lower the value of the Peclet number, the closer the well-mixed condition will be approached. If the Peclet number is in the intermediate range, say, $0.1 < N_{pe} < 20$, then neither of the above mentioned idealized situations obtains. In this intermediate region, the axial dispersion model may be used. In general, the yield for a reactor with higher Peclet number is higher than that with lower Peclet number. This can be seen from Cases D & E where both the gas phase and liquid phase Peclet number in the dissolver section were chosen as 0.1, and the mass transfer coefficients were chosen respectively as equal to Cases A and C. The coal liquefaction yield for Case D is 89.1%, which is about 2.9% lower than that for Case A; for Case E the coal dissolution is 82%, which shows a 3.5% decrease compared to Case C. The Peclet numbers for both Cases A & C are $N_{pe,l} = 0.97$ and $N_{pe,g} = 4.66$. From the above comparisons, we see that the effect of Peclet number on coal dissolution becomes more significant when the mass transfer coefficient is low.

The detailed concentration profiles are given in Figs. 1-4. Figs. 1 and 2 show the hydrogen concentration profile in the vapor phase and liquid phase, respectively, along the reactor. The coal concentration, $C_c = C_{c1L} + C_{c2L}$, profiles are shown in Fig. 3, and also shown in Fig. 4 is the organic sulfur concentration, $C_s = C_{s1L} + C_{s2L}$, profiles. The yields of coal liquefaction, hydrodesulfurization and hydrogen consumption rate for Cases A to E are also tabulated in Table 2.

In addition to the above five cases, cases for which the mass transfer coefficient was twice and ten times that of Case A were also simulated. The results showed that the hydrogen consumption and coal dissolution were not significantly different from Case A. This implies that the Wilsonville SRC pilot plant is already operating in a kinetically limited regime and that mass

transfer is not the rate controlling step. These two cases were not plotted on Figs. 1-4 because they were essentially indistinguishable from Case A. This result is reasonable, since no external catalyst, other than the naturally occurring coal mineral matter, is present in the SRC reactor. It is known, however, that coal minerals can and do catalyze both hydrogenation and desulfurization reactions in the SRC process (Henley, et al, 1976; Prather, et al, 1976; Guin, et al, 1977). Under operating conditions near those of Case A studied here, the organic sulfur removal and the hydrogen consumption at the Wilsonville SRC pilot plant averaged around 50% and 2% based on weight of maf coal feed, respectively. As observed from Table 2, the corresponding values from the model are about 50% lower than those determined experimentally in the Wilsonville SRC pilot plant under apparently similar operating conditions. There are two reasonable explanations for this deviation. First, it should be noted that in the present model the hydrogen consumption only includes the actual amount of hydrogen chemically reacting in the preheater and dissolver, i.e., no other losses such as from flash systems, waste vents, incomplete separations, leaks, etc., are included. Secondly and perhaps more importantly, it has been observed that because of the very low upward liquid velocity, an accumulation of coal mineral matter occurs in the Wilsonville SRC reactor. This would cause increased desulfurization and hydrogenation because of the catalytic nature of these minerals. Recent lower hydrogen consumption with an initially clean reactor at Wilsonville tends to verify this latter result. Also it has recently been shown (Guin, et al, 1977), that the addition of iron compounds, predominant in coal minerals, can increase the extent of organic sulfur removal by around 100%. Finally, it should be noted that the kinetics rate expressions used herein are strictly valid only for the Kentucky 9/14 coal with a creosote oil solvent. For other coals and solvents, different rate expressions would be required for the most accurate results.

CONCLUSIONS

1. The mixing and flow pattern of the multi-phase reactor is taken into account through the axial dispersion term, which has not been previously utilized for the SRC reactor modeling.
2. The mass transfer of hydrogen from the gas phase into the liquid phase is also accounted for in the model, the effect of hydrogen mass transfer rate on the hydrogen consumption and coal dissolution rate can be easily simulated; and the influence and extent of mass transfer control can be assessed. In particular, the Wilsonville SRC reactor is found to operate in a kinetically, rather than a mass transfer limited regime.
3. All of the parameters arising in the model are obtainable independently from literature correlation; these parameters have definite physical meanings based upon the flow conditions, therefore, by changing the relative magnitude of each parameter, the general trend of the effect of each operating variable on the SRC process can be assessed, thus providing a better engineering design basis for simulation and optimization of the SRC process.
4. The hydrogen consumption and organic sulfur removal at the Wilsonville SRC pilot plant are higher than predicted by the present model, which uses kinetics rate expressions from laboratory experiments. This is probably due to the accumulation of catalytic coal minerals in the Wilsonville reactor, giving higher rate constants.

Nomenclature:

D_g	gas phase axial dispersion coefficient
D_L	liquid phase axial dispersion coefficient
v_{slip}	two phase slip velocity
v_g	bubble phase velocity, m/sec
v_L	liquid phase velocity, m/sec
v_{gs}	bubble phase superficial velocity, m/sec
v_{ls}	liquid phase superficial velocity
τ_g	gas holdup
a	specific gas-liquid interfacial area
Pe_g	$= \frac{v_g(L-z_1)}{D_g}$, gas phase Peclet number in the dissolver section
Pe_L	$= \frac{v_L(L-z_1)}{D_L}$, liquid phase Peclet number in the dissolver section
z_1	length of preheater plus transfer line section
z_2	length of dissolver
x_1	dimensionless axial length of preheater plus transfer line z_1/L
x	dimensionless axial coordinate, z/L
K	liquid phase mass transfer coefficient
K_{Ca}	volumetric liquid phase mass transfer coefficient
z	coordinate in the axial direction
H_o	Henry's law constant of hydrogen in creosote oil
c_{ij}	feed concentration of component i in phase j
L	total length of reactor, $L = z_1 + z_2$
C_{ij}	$= c_{ij}/(H_o c_r)$ dimensionless concentration for i th component in the j phase
c_{ij}	concentration of component i in the j phase
c_r	reference concentration

Superscript:

o	denotes initial condition
I	in the preheater section
II	in the dissolver section
k	$= 0$ for gas phase; $= 1$ for liquid phase

Subscript:

g	gas phase
L	liquid phase

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TABLE 1 Values of Parameters Appearing in Design Equations for Cases A, B, C, D and E

Parameters Cases	$K_{CL}/\Delta G_H$		K_{CL}/\hat{V}_L		$k_{H_2L}(1-f_g)/\hat{V}_L$		$[k_{CL}(1-f_g)/\hat{V}_L] \left(\frac{C_r}{H}\right)^2$	
	Preheater	Dissolver	Preheater	Dissolver	Preheater	Dissolver	Preheater	Dissolver
A	10.33	104	139.2	137.4	2.878×10^2	14.4	1.343×10^3	2.369×10^5
B	1.033	10.4	13.92	13.74	2.878×10^2	14.4	1.343×10^3	2.369×10^5
C	0.207	2.08	2.78	27.48	2.878×10^2	14.4	1.343×10^3	2.369×10^5
D	10.33	104	139.2	137.4	2.878×10^2	14.4	1.343×10^3	2.369×10^5
E	0.207	2.08	2.78	27.48	2.878×10^2	14.4	1.343×10^3	2.369×10^5

Parameters Cases	$\left[\frac{k_{G_2L}(1-f_g)/\hat{V}_L}{\left(\frac{C_r}{H}\right)^2} \right]$		$K_{S_1L}(1-f_g)/\hat{V}_L$		$k_{G_2L}(1-f_g)/\hat{V}_L$		$N_{Pe,g}$	$\eta_{Pe,L}$	C_r
	Preheater	Dissolver	Preheater	Dissolver	Preheater	Dissolver			
A	35.2	2.283×10^4	1.8×10^{-2}	67.35	1.68×10^{-3}	0.941	4.66	0.97	0.141
B	35.2	2.283×10^4	1.8×10^{-2}	67.35	1.68×10^{-3}	0.941	4.66	0.97	0.141
C	35.2	2.283×10^4	1.8×10^{-2}	67.35	1.68×10^{-3}	0.941	4.66	0.97	0.141
D	35.2	2.283×10^4	1.8×10^{-2}	67.35	1.68×10^{-3}	0.941	0.1	0.1	0.141
E	35.2	2.283×10^4	1.8×10^{-2}	67.35	1.68×10^{-3}	0.941	0.1	0.1	0.141

TABLE 2. Calculated Yields for the SHC Process

	Case A	Case B	Case C	Case D	Case E
	92%	90.7%	85.5%	89.1%	82%
Coal liquefaction yield					
Organic sulfur removal	25%	25%	25%	23.9%	23.9%
Hydrogen consumption (g H ₂ /g maf coal)	0.87%	0.82%	0.61%	0.66%	0.50 %

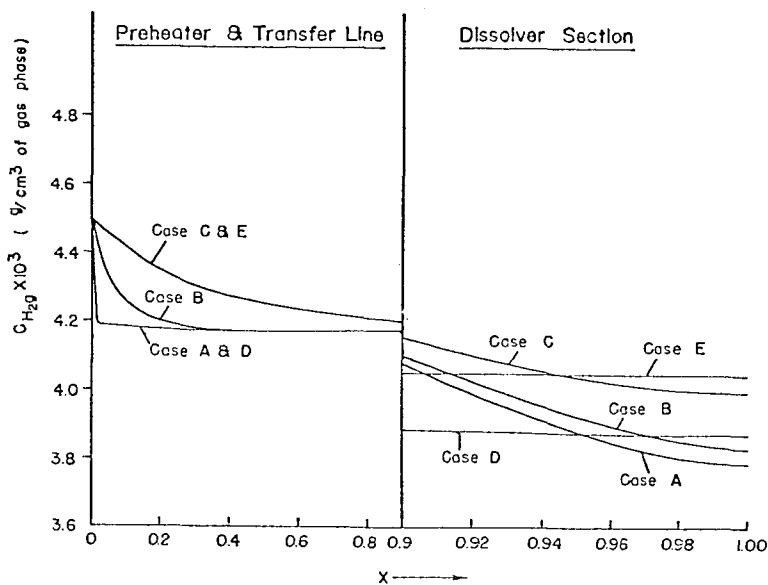


Figure 1. Vapor Phase Hydrogen Concentration vs. X

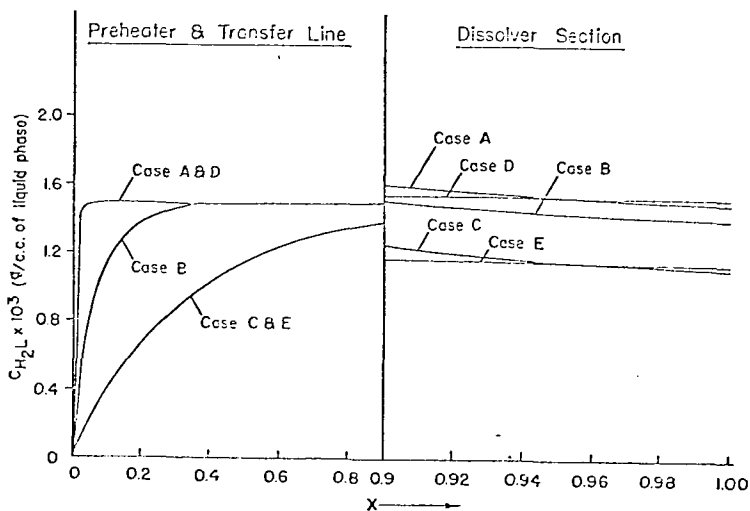


Figure 2. Liquid Phase Hydrogen Concentration vs. X

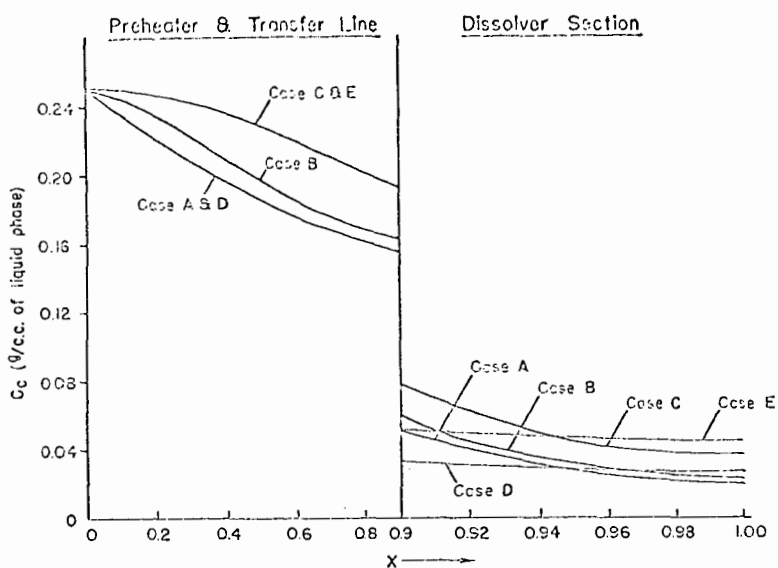


Figure 3. Coal Concentration vs. X

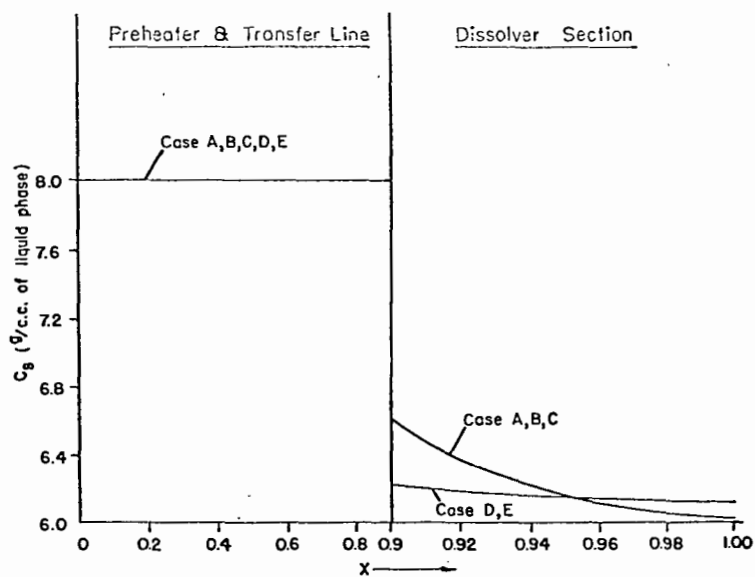


Figure 4. Sulfur Concentration vs. X

CONTINUOUS LIQUEFACTION OF LIGNITE IN A PROCESS DEVELOPMENT UNIT

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INTRODUCTION

The decline in domestic production and reserves of petroleum and natural gas has highlighted the necessity of supplemental sources. Presently nearly 50 percent of our petroleum requirements are imported, a situation which is economically and politically dangerous. A major source of replacement energy is our abundant coal reserves. Direct utilization of most coals is environmentally unacceptable, and in many applications the solid form is not suitable for use and liquid or gaseous phases are required.

Conversion of coal to liquid or gaseous fuels can be accomplished by hydrogenation to increase the H to C ratio. Direct liquefaction from coal without gasification and synthesis steps allows reduced hydrogen requirements, fewer process steps, and consequently, lower costs.¹ Ash and sulfur contents can be reduced and heating value per unit weight increased. A low polluting solvent refined coal or synthetic fuel oil could be used in stationary power generating facilities. Liquid fuels suitable for use in mobile transportation can be produced by additional hydrogenation.

Many hydrogenation-liquefaction processes have been proposed for coal. Most supported research on liquefaction has been directed toward high rank coal and has been summarized by Friedman et al.¹ A modification appropriate for hydrogenation of low rank coals is the use of carbon monoxide in the presence of a hydrogen donor solvent.² Natural moisture content in the low rank coal is more effective than added moisture. Synthesis gas (H_2 and CO) also gives high conversion and is less expensive than either pure carbon monoxide or hydrogen.³ Although naturally occurring ash constituents in the lignite are known water gas shift reaction catalysts, the contribution of carbon monoxide seems to be more complex than this and is ash catalyzed.⁴ Carbon monoxide appears to be effective because of removal of a source of cross linkage rather than by bond cleavage.

Initial work on liquefaction of lignite at the University of North Dakota was batch autoclave tests under sponsorship of the Burlington Northern Railroad. A major expansion occurred in 1972 when a five year, research contract was signed with the U.S. Office of Coal Research (now the Energy Research and Development Administration). Extension of the contract is being negotiated.

The present paper reviews the operation of a 0.6 ton/day process development unit (PDU) for continuous liquefaction of lignite at 1500-2500 psig and 700-950°F in an atmosphere of synthesis gas in the presence of a hydrogen donor solvent. Solvent recovery and solvent recycle capabilities are provided as well as process gas clean up and recycle. Ash is removed by dilution of vacuum flash bottoms with toluene followed by settling to remove ash and unreacted lignite. The deashed solvent refined lignite (SRL) is recovered by distilling the toluene for recycle from the extract. The SRL, a solid at room temperature, is low in ash, has a reduced sulfur content, a high calorific value, and would be environmentally acceptable for particulate and SO_x emissions upon combustion.

Hydrogenating sufficiently to produce SRL at high conversion can be done in an atmosphere of synthesis gas by making use of the natural catalyst activity of the lignite without the use of very high pressures. The SRL is a superior raw material for additional hydrogenation to liquids for fuels or as a source of organic chemicals. While the natural catalytic activity favors initial hydrogenation solution, increased hydrogenation can be better accomplished using a specific hydrogenation catalyst. Removal of ash constituents which could poison the hydrogenation catalyst makes the concept of two stage hydrogenation attractive in that both steps can be optimized and more effective overall hydrogenation can be achieved.

PROCESS DEVELOPMENT UNIT

The Project Lignite Process Development Unit has a nominal design capacity of 50 pounds of raw lignite feed per hour and produces approximately 15 pounds per hour of solvent refined lignite (SRL) with a melting point of 300-400°F as well as additional quantities of lighter liquids and gases.

Pulverized lignite of full moisture content is slurried with solvent. The slurry is pressurized, preheated and reacted at selected temperature and pressure in a reducing gas atmosphere. The products are then separated as gases, liquids, and SRL from the unreacted coal and mineral matter. A simplified block flowsheet of the process is presented in Figure 1.

Asreceived lignite is first split into representative samples using a rail car-size sample splitter and stored in nitrogen-purged bins until needed. The lignite is crushed and pulverized to 100 percent passing 60 mesh and 90 percent passing 200 mesh Tyler screens. After pulverization, the lignite is stored in 55-gallon drums prior to slurry preparation.

The pulverized lignite is blended in a slurry mixing tank

with recycle liquefaction solvent. For startup, a petroleum-derived solvent having a boiling range of 212° to 446°F at 1.6 mm Hg absolute is used. The slurry is continuously pumped through a recirculating loop to maintain suspension. A side stream is pumped to high pressure, mixed with hydrogen and/or carbon monoxide gas, and is heated to reaction temperature in an electrically heated, fluidized-solids preheater. Most operations are in the range of 700°F to 850°F at 1500-2500 psi. Upon leaving the preheater, the mixture enters the dissolvers (R-1A and R-1B) where reaction temperatures are maintained and sufficient residence time provided for solvation. The two dissolvers can be used in series or separately. Operations are usually with a single dissolver. The undissolved material consists of unreacted lignite and inorganic mineral matter. Upon leaving the dissolvers, the non-condensable gases and light hydrocarbon vapors are separated from the slurry in a series of five separation vessels in which pressure and temperature are decreased in stages.

The PDU is designed so that solvent can be recycled without operating the solid-liquid separation area. In this mode of operation, the slurry after gas separation and pressure letdown is heated to approximately 600°F in a Dowtherm preheater followed by vacuum flash distillation. Volatile liquids and solvent are separated from the vacuum bottoms which contain the mineral residue, undissolved lignite and solvent refined lignite. The overhead stream is condensed, combined with another light liquid stream from the primary separators, and fed to a second Dowtherm preheater preceding the main solvent recovery fractionators. In the fractionator, light ends, liquefaction solvent and heavy ends are separated. The liquefaction solvent is recycled.

The non-condensable gases from the primary high pressure separators are channelled through the gas recovery area; carbon dioxide and hydrogen sulfide are removed, and a portion of the hydrogen and carbon monoxide gas is recycled.

When the solid-liquid separation system is in use, an initial partial vacuum flash vessel (F-0) is used to remove part of the liquefaction solvent from the separator effluent. The bottoms are pumped to a mixing-surge vessel and mixed with toluene (2:1 by volume). The mixture is pumped to a gravity settling tower (V-8) operating above the critical pressure but slightly below the critical temperature of toluene. Additional wash toluene is fed counter-currently to the direction of settling. The dissolved SRL, the remainder of the liquefaction solvent and toluene are withdrawn from the top of the settler and passed into a vessel (V-9) in which the toluene is removed by flash distillation. The toluene is recycled and the SRL plus liquefaction solvent recovered. The SRL solvent stream is passed through Dowtherm preheater E-11 and into the vacuum flash drum F-1. The SRL is recovered as the bottoms from this vessel and the overhead liquefaction solvent stream is combined with the partial flash (F-0) overhead as feed to the light ends column (F-2). The F-2 bottoms are sent back to the slurrymix tank as recycle solvent.

TYPICAL OPERATING CONDITIONS AND RESULTS

During steady operation of the PDU, which is normally operated continuously for a five-day week, material balances are made over yield periods of twelve hours duration. Fresh containers are used for the products during a yield period, and samples and operating data are collected throughout the period.

In the following discussions, material balance and yield data are presented for Run Period M-17A, flows being expressed in pounds per hour averaged over the twelve hour yield period. Test conditions for this run are close to the optimum obtained thus far. The solid-liquid separation unit using toluene as deashing solvent was also in operation during this run.

Operating rates and stream ratios are given in Table 1. Lignite at 45 lb/hr was slurried with 81 lb/hr recycle solvent and mixed with 531 SCFH of feed gas containing 76 percent hydrogen and 24 percent carbon monoxide. In the solid-liquid separations area, 112 lb/hr of toluene was used to extract product SRL and liquefaction solvent from unconverted solids.

Operating temperatures and pressures for various process vessels, identified as coded in the flow sheet (Figure 1), are presented in Table 2. Operating pressure in preheater and dissolver was 2500 psig, and slurry left the preheater at 747°F and reached 802°F in the dissolver. There is usually a 50 to 100°F temperature rise in the dissolver due to the exothermic overall reaction. A single reactor (R-1A) having a reaction volume of 1.42 cu ft was used. In ash separation, the toluene settling tower was operated at 378°F and 300 psig, and the vacuum flash unit maintained at 626°F and 15 Torr.

Source and characteristics of lignite, reacting gases and starting solvent are given in Table 3. The lignite was charged at 31.5 percent moisture. The as-mined moisture was probably around 37 percent, and transportation, crushing and handling were done in such a way as to minimize moisture loss. Feed gas was supplied from tank trailers of pure hydrogen and carbon monoxide and mixed just before entering the compressor. The startup solvent was Gulf FS-120, a petroleum derived catalytic cracker recycle stock. Comparison of its boiling ranges fractions with those of recycle solvent during the run shows a tendency of the solvent to lighten on continued recycle.

The gross input and output material balances are shown in Figure 2, in which the magnitude of the two recycle streams are compared with the coal and gas processed. For each pound of input lignite, 0.26 lb of syngas, 1.8 lb of liquefaction solvent and 2.5 lb of toluene deashing solvent were circulated.

The net material balance based on lignite and syngas fed is shown in Figure 3. In this run, per 100 pounds of MAF lignite charged, 54 pounds of SRL and 13 pounds of light organic liquids were produced.

Table 4 gives net yields of products both in lb/hr and in lb/100 pounds MAF lignite. There is a net consumption of 5.9 percent of water, and 67.3 percent of the MAF lignite is converted to SRL and light organic liquids. Conversion was 89.4 percent although conversions as high as 95 percent have been obtained in some runs.

Table 5 presents gas amounts in and out as volume percent gas composition and as lb/hr. Note that 38 percent of the entering CO was consumed as compared to only 14 percent of the entering hydrogen, and that 0.67 moles of CO₂ appear in the exit gas per mole of CO charged, or 1.77 moles of CO₂ per mole of CO consumed.

Some of the characteristics of the product SRL are given in Table 6. In Run 17-A, flow rates were satisfactory in the solid-liquid separations system, but problems with the solids removal system in the settling tower V-8 prevented removal of the unconverted coal and mineral matter, which therefore carried over to some extent into the SRL product. Thus in Table 6 actual vacuum bottoms composition and properties are shown, along with the analyses that would have been obtained had the solids been properly removed.

Ultimate analysis of lignite, starting and recycle solvent, and SRL product are shown in Table 7. The coal-derived material contains a substantial amount of oxygen, 5.7 percent in the SRL and 5.1 percent in the recycle solvent. The startup solvent has built up from 0.5 percent oxygen to 5.1 percent in the recycle solvent, showing that compounds formed from the coal have replaced much of the starting solvent. A large amount of this oxygen is present as phenolic compounds.

CORRELATIONS OF OPERATING VARIABLES

Data from 18 runs, from the series of runs M-1 through M-23 that resulted in usable yield periods, are summarized in Tables 8, 9, and 10. Correlations and curves developed from these data are presented in Figures 4 through 11, using symbols identified in the tables.

The influence of maximum dissolver temperature on yield characteristics is presented in Figure 4 at a 1/1 H_2/CO ratio, 2500 psi, and for a limited range of liquid hourly space velocities and solvent to lignite ratios. Conversion, as to be expected, increased with increased temperature. However, yield of light oil plus SRL decreased slightly over the temperature range investigated. The major change was in increased production of gases indicating additional degradation of the lighter fractions. Little change was evident in utilization of moisture by reaction.

The slopes of the lines of Figure 4 were used to establish temperature coefficients which were then used to adjust all yield data to the same maximum dissolver temperature of 826°F. These adjusted data are plotted in Figure 5 versus liquid hourly space velocity. Increased liquid space velocity corresponds to reduced residence time of the lignite-solvent slurry in the dissolvers. Consequently, conversion is reduced, although only slightly, for about a 40 percent increase in space velocity. Less degradation of liquefaction products is indicated by an increase in oil yields and a decrease in gaseous products. Water consumption was nearly constant for the conditions tested.

The data of Figure 5 were further adjusted to a constant LHSV of 1.425, then plotted as a function of solvent/coal ratio in Figure 6. Yields increased uniformly with increasing solvent/lignite ratio from 1.6 to 2.3. Consumption of water as a "hydrogenation" source also increased. Over the range of gas charge rates used, there appeared to be no significant effect of either gas rate or gas to coal ratio.

Sufficient data have been accumulated at 2500 psig and a 1/1 H_2/CO ratio to utilize regression analysis to obtain equations relating yields to the operating variables of maximum reactor temperature, liquid hourly space velocity, and solvent/MAF lignite weight ratio. These equations should be quite useful in visualization of the effects of process variables, and are summarized on the following page.

$$\text{Percent Net Gas} = 204.971X_1 - 15.110X_2 + 8.835X_3 - 228.615$$

$$\text{Percent Net Oil} = -26.505X_1 - +8.450X_2 + 8.272X_3 + 71.759$$

$$\text{Percent Net H}_2\text{O} = -37.225X_1 - -4.461X_2 - 9.724X_3 + 63.617$$

$$X_1 = \text{Temperature Variable, } \frac{\text{Temp., } ^\circ\text{F} + 460}{1000}$$

$$X_1 = \text{LHSV, Hr}^{-1}$$

$$X_3 = \text{Solvent/MAF Coal Weight Ratio}$$

Solvent recovery is critical to the liquefaction process. Suitable solvent must be generated from the coal substance during liquefaction and recovered to replace losses. Information concerning solvent recovery is given in Figure 7 as a function of maximum dissolver temperature. Shown in the lower half of Figure 7 is the total solvent accounted for. The line represent the average of the calculated total solvent production at 2500 psig. The total is over 100 percent, indicating that a net production of solvent range material is possible. However, the effective solvent, i.e., that boiling from about 550°F to 850°F equivalent temperature at atmospheric pressure, seems to reach a maximum with a slight net production around 820°F maximum dissolver temperature, but falls below 100 percent at temperatures below 800°F or above 835°F, as shown in the upper half of Figure 7.

The runs made at lower pressures, either 1500 or 2000 psig, regardless of H₂/CO ratio, result both in lower total oil and in lower effective solvent production. In all cases the yields were less than 100 percent of the solvent charged which indicates a net solvent consumption, probably because of higher conversion to gas. With other ratios of H₂/CO at 2500 psig the yields were not greatly different from those with a 1/1 H₂/CO ratio. With 1/3 H₂/CO ratio, the effective solvent recovered was about the same as with 1/1, though the total oil was slightly less, because of relatively less light oils. With 3/1 H₂/CO the total oil recovery was greater than with 1/1, though the effective solvent recovery was less because of increased production of light oils.

The data for runs at 3/1 H₂/CO ratio, adjusted to a constant dissolver temperature, LHSV and solvent to coal ratio are presented in Figure 8. The pressure has little effect on gas yield, but increasing pressure results in increasing conversion and even more rapidly increasing oil yields. At lower pressures there is a net make of water, but at higher pressures water is consumed, the consumption increasing rapidly with pressure. This results in increasing yields of light oil and SRL.

The solvent recovery data for the 3/1 H₂/CO runs are presented in Figure 9. At this ratio effective solvent recovery is less than 100 percent even at 2500 psig, though the total oil recovery is over 100 percent because of the relatively

higher light oil yield obtained at higher hydrogen concentration.

The yields resulting from several runs made at 2500 psig and varying H_2/CO ratio were adjusted to constant parameter values as indicated in Figure 10 and plotted against mole percent hydrogen in the charge gas. The data indicate an optimum at about 50 to 60 percent hydrogen. One run made with pure hydrogen (M-20) resulted in relatively low conversion and oil yield. However, this run was made at such a high temperature that coking and/or repolymerization may have significantly affected the results.

Solvent recovery data are similarly plotted versus mole percent hydrogen in Figure 11. The optimum also appears to be near 60 percent hydrogen.

The use of lignite containing its natural moisture (about 30 weight percent as charged to the PDU) and synthesis gas containing carbon monoxide results in substantial production of carbon dioxide. The product gas also contains light hydrocarbons resulting from the breakdown of the coal substance and of the solvent. The yields of carbon dioxide and of C1 to C3 hydrocarbons seem to be essentially linear functions of maximum dissolver temperature for the 2500 psig 1/1 H_2/CO operations. Variables other than temperature seem to have little effect. The yields of C1 to C3 hydrocarbons range from almost zero at 760°F to about 12 weight percent of the MAF lignite at 880°F, while CO_2 yields range from about 12 weight percent of the MAF lignite to 65 percent over the same temperature interval. Lower pressures and 3/1 or 1/3 H_2/CO ratios have little effect on C1 to C3 hydrocarbon yields. At the higher temperatures decreasing the amount of CO decreases CO_2 yields, while increasing CO increases CO_2 yields. One run made with pure hydrogen resulted in a very low CO_2 yield and a high gas yield, but again this was at such a high temperature level that other effects may also have become significant.

It now appears that for this particular reactor configuration and limitations, optimum results will be obtained at 2500 psig with 50 to 60 percent hydrogen in the charge gas using one reactor corresponding to a liquid (slurry) hourly space velocity of about 1.4. The effects of solvent/coal ratio have not been evaluated completely, but it appears that the lower the ratio the better the solvent recovery, which means that the thickest slurry that can be handled should be charged.

PLANS FOR FUTURE WORK

The Project Lignite work has been extended for an additional year to continue the development of the process. The effort will be concentrated on proving the operability of the unit in runs of longer duration and in evaluating the solid-liquid separations system.

A series of three one-month long runs is planned over a 6-months period to establish the effects of continuing to recycle the lignite-derived process solvent and demonstrate the self-sufficiency of the process with respect to liquefaction solvent. The gas cleanup and recycle section will be operated on at least one extended run to determine makeup gas requirements and the effect of any impurities remaining in the recycle gas. The solid-liquid separations system will be operated integrally with the PDU to produce clean SRL.

As a part of this program, prestressed test coupons will be placed in process streams to determine their susceptibility to corrosion in the process environment. An attempt will also be made to study the buildup of solids in the dissolver, a problem that has serious implications for long-term steady operation of the PDU. The rate of buildup and composition will be determined and means of alleviating the problem will be considered.

The long runs should also provide a means of producing substantial amounts of clean SRL for evaluation by other ERDA contracts for various end uses.

A longer range goal of the investigation, not included in the current extension, is the hydrotreating of SRL to hydrocarbon liquids. This has been carried out in the laboratory but removed from the PDU program. Certain other programs should also be carried out including modified dissolver design, hydrotreating of recycle solvent, and testing of other coals in the process. In general, the PDU is a useful developmental tool that could test many innovations in process technology in the upgrading of lignite.

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April 30, 1977

TABLE 1 - OPERATING RATES AND RATIOS

Lignite (31.5% Moisture)	44.75 lb/hr
Gas (24% CO, 76% H ₂)	11.54 lb/hr
	531 SCFH
Liquefaction Solvent	81.3 lb/hr
Deashing Solvent (Toluene)	111.9 lb/hr
Ratios and Space Velocities	
Slurry rate, LHSV	1.34 hr ⁻¹
Gas Rate (in SCF)	374 hr ⁻¹
Solvent/coal ratio	1.82
Toluene/slurry ratio	3.6 (approx.)

TABLE 2 - OPERATING TEMPERATURES AND PRESSURES

	Temp ^o F	Pressure, psig
Dissolver Preheater E-1 Inlet	289	2500
Outlet	747	2500
Dissolver R-1A from Bottom 3 ft	752	2500
7 ft	779	2500
11 ft	793	2500
15 ft	802	2500
Separators S-1	574	2500
S-2	76	2500
S-3	479	250
S-4A	78	60
Partial Flash F-0 Overhead	471	15 Torr
Bottoms	340	15 Torr
Vacuum Flash F-1 Vapor	554	15 Torr
Upper Wall	626	15 Torr
Solids-Liquids Settling Tower V-8	378	300 psig
Toluene Recovery Tower V-9	444	2 psig

TABLE 3 - FEED MATERIALS

Lignite

North American Coal Co., Zap, N.D.
Screen size 90%-200 mesh, 100%-60 mesh
Moisture: 31.5%

Ultimate Analysis (% Wt)

C	46.21
H	6.42
N	0.66
S	0.44
O (diff)	40.54
Ash	5.73

Feed Gas (mixed from tank trailers)

	% Vol.	% Wt.
CO	24.0	81.4
H ₂	76.0	18.6

Startup liquefaction solvent

Gulf Oil Co.	FS-120 cat.	cracker recycle	stock
Boiling range (1.6 Torr)	FS-120	Recycle	
	Startup	Solvent	
0-100°C	5.0%	30.0%	
100-230°C	83.6	57.7	
230-255°C	11.4	11.8	
Specific Gravity	1.043	0.988	

TABLE 4 - NET YIELD OF PRODUCTS

	<u>lb/hr</u>	<u>lb/100 lb MAF Lignite</u>
Gas	7.87	28.0
Light Oil (0-100°C at 1.6 Torr)	1.42	5.1
Liquefaction Solvent (100-230°C at 1.6 Torr)	1.71	6.1
Heavy Oil (230°-255°C at 1.6 Torr)	0.56	2.0
SRL	15.21	54.1
Unreacted Lignite	2.99	10.2
Water Consumed	1.67	5.9

TABLE 5 - GAS MATERIAL BALANCE FOR GAS COMPONENTS

	<u>Vol % In</u>	<u>Vol % Out</u>	<u>lb/hr In</u>	<u>lb/hr Out</u>
H ₂	76.2	66.2	2.15	1.84
CO	23.8	14.7	9.39	5.79
CO ₂	-	13.8	-	9.93
H ₂ S	-	0.1	-	0.13
CH ₄	-	3.8	-	0.93
C ₂ H ₆	-	1.0	-	0.52
C ₃ H ₈	-	0.2	-	0.22
NH ₃	-	0.03	-	0.04

TABLE 6 - ANALYSIS OF PRODUCT SRL

	<u>F-1 Vacuum Bottoms (measured)</u>	<u>SRL (calculated)</u>
Boiling Range Fraction, wt % 255°C (1.6 Torr)	0	0
SRL	77.22	100.0
Unconverted Coal, wt %	15.30	0
Ash, wt %	7.48	0
Gradient Bar Melting Point °F	327°	-
Pyridine Solubles, wt% ash-free	83.5	100
Specific Gravity	1.28	1.25
Heat of Combustion, Btu/lb	14,330	15,990

TABLE 7 - ULTIMATE ANALYSIS OF MATERIALS

	<u>Lignite Charged</u>	<u>Starting Solvent</u>	<u>Recycle Solvent</u>	<u>Vacuum Bottoms</u>	<u>Deashed SRL</u>
C	46.21	89.05	83.56	80.09	86.56
H	6.42	8.12	9.84	5.26	5.69
N	0.66	0.14	0.21	0.95	1.03
S	0.44	2.19	1.27	0.94	1.02
O*	40.54	0.50	5.12	5.28	5.70
Ash	5.73	0	0	7.48	0

*By difference

Table 8-- Summary of Liquefaction Tests (1/1 H₂/CO)

Yield Period Symbols	M-1C	M-2A	M-2C	M-3B	M-5A	M-5B	M-5C	M-5D	M-8C	M-9C
Hours on Coal at End of Y.P.	62	25	73	38	19	43	55	67	39	43
During Run	62	87	135	173	227	251	263	275	358	422
Cumulative	2	2	2	1	1	1	1	1	1	1
No. of Reactors	53	53	61	50	58	47	46	51	54	47
Coal Charged, lbs/hr	471	458	454	414	399	426	483	379	449	459
Gas Charged, SCF/hr	2.30	2.18	2.06	1.89	1.59	1.80	1.92	1.97	1.62	1.91
Solvent/Coal Ratio	0.90	0.86	0.95	1.48	1.54	1.33	1.38	1.51	1.40	1.41
LHSV, Hr ⁻¹	164	160	159	289	279	299	334	265	314	321
GHSV, Hr ⁻¹	18.6	18.5	21.2	35.2	40.8	32.6	32.4	36.0	37.5	32.9
Coal Rate, Lbs/Hr/CF	8.8	8.6	7.5	8.2	6.8	9.2	10.4	7.4	8.4	9.8
Gas Rate, SCF/Lb Coal	2.9	2.9	1.2	2.4	0.5	0.8	1.5	1.9	1.3	1.9
Gas Consumed, SCF/Lb Coal										
Yields, Wt % MAF Coal										
Net Gas	10.4	12.4	9.7	25.2	35.6	35.5	36.7	32.9	28.2	15.9
Net Oil	58.1	69.1	50.2	58.3	55.9	62.0	68.0	65.1	61.5	66.8
(Light Oil)					(8.9)		(9.6)	(11.0)	(4.9)	(9.5)
(SRL)	(58.1)	(69.1)	(50.2)	(58.3)	(47.0)	(62.0)	(58.4)	(54.1)	(56.6)	(57.3)
Net H ₂ O + Ash	3.7	-0.6	2.7	-2.6	-7.5	-8.8	-14.1	-12.0	-4.4	-4.4
Unconv. MAF Coal	27.8	19.1	37.4	19.1	16.0	11.3	9.4	14.0	14.6	21.7
Solvent Recycle, %										
Actual	85.9	64.1	87.2	83.1	90.2	93.5	94.7	95.1	99.9	89.2
Possible (Calc.)	98.6	97.2	96.4	98.0	103.7	99.6	103.3	103.7	102.0	103.2
Material Balance, %	100.0	103.4	97.7	98.8	94.7	97.8	95.5	97.8	98.1	99.7
Conditions										
Temperatures, °F										
Preheater Outlet	702	733	698	746	754	748	750	742	730	753
Dissolver Inlet	-	-	-	700	749	731	768	762	693	726
R-1A 3 ft	708	714	663	738	NIU	NIU	NIU	NIU	NIU	NIU
R-1A 15 ft	748	760	699	797	NIU	NIU	NIU	NIU	NIU	NIU
R-1B 3 ft	716	735	675	NIU	815	778	797	786	755	777
R-1B 15 ft	735	752	690	NIU	872	820	841	844	817	768
Dissolver Outlet	-	-	-	804	886	826	845	850	-	778
Flash Preheat	594	583	552	626	603	627	626	627	608	620
Flash Vapor	572	538	528	568	574	544	538	537	575	552
Pressures, psig										
Dissolver	1500	1500	1500	2000	2500	2500	2500	2500	2500	2500
Inter-Sep.	350	350	312	300	250	250	250	250	250	400
Vac. Flash, Torr	10	6	6	14	12	10	10-15	11	10	15
S-LS System in Use?	No	No	No	No	No	No	No	No	No	Yes

Table 9 - Summary of Liquefaction Tests (1/1 H₂/CO)

Yield Period Symbols	M-10A	M-10B	M-10C	M-10D	M-10E	M-11A	M-11B	M-11C	M-11D	M-12A	M-13A	M-13B	M-13AB	M-14A	M-14C	M-15A	M-15B	M-15AB
Hours on Coal At End of Y.P.	34	55	67	79	36	51	70	86	30	42	57	57	23	60	23	23	35	35
During Run	461	482	494	506	562	557	576	592	626	717	732	732	782	819	842	854	854	854
Cumulative	1	1	1	1	1	1	1	1	1/2	1	1	1	2	1	1	1	1	1
No. of Reactors	49	49	48	47	23	23	32	25	22	26	24	25	40	41	48	44	46	46
Coal Charged, lbs/hr	499	422	478	463	439	436	459	463	466	479	489	487	467	500	482	467	475	475
Gas Charged, SCF/hr	1.91	1.71	2.26	1.83	2.01	2.08	2.15	1.95	2.18	2.09	2.28	2.18	3.00	2.03	1.78	1.96	1.86	1.86
Solvent/Coal Ratio	1.46	1.37	1.60	1.37	0.74	0.72	0.99	0.76	1.44	0.85	0.81	0.83	0.84	1.27	1.33	1.38	1.36	1.36
LHSV, Hr ⁻¹	349	295	335	324	307	305	318	324	651	334	341	338	163	349	338	327	332	332
GHSV, Hr ⁻¹	34.0	34.4	33.3	32.8	16.3	16.0	22.5	17.3	31.1	18.4	16.5	17.5	14.0	28.5	33.4	31.0	32.2	32.2
Coal Rate, lbs/hr/CF	10.3	8.6	10.0	9.9	18.8	19.1	14.3	18.7	21.0	18.2	20.7	19.5	11.6	12.3	10.1	10.5	10.3	10.3
Gas Rate, SCF/lb Coal	2.9	2.7	2.1	2.3	9.9	7.2	6.3	6.4	0.4	2.2	3.5	2.9	4.2	3.6	0.7	1.7	1.7	1.7
Gas Consumed, SCF/lb Coal																		
Yields, %: % NAP Coal																		
NAP Gas	33.8	27.5	30.4	21.3	63.0	40.1	55.7	36.5	20.7	34.3	44.4	38.6	51.5	44.1	27.3	25.0	26.1	26.1
NAP Oil	64.1	69.1	75.3	75.1	37.5	63.1	43.5	82.3	61.9	65.3	64.7	69.7	50.2	60.2	46.9	47.0	47.0	47.0
(Light Oil)	(2.7)	(12.6)	(0.5)	(18.7)	(1.7)	(16.4)	(6.3)	(16.7)	(6.1)	(3.8)	(8.2)	(10.3)	(3.9)	(4.9)	(10)	(0)	(0)	(0)
(SHL)	(61.4)	(58.5)	(74.8)	(56.4)	(35.8)	(46.7)	(37.2)	(45.6)	(55.8)	(61.7)	(56.5)	(59.4)	(46.3)	(55.3)	(46.9)	(47.0)	(47.0)	(47.0)
Net H ₂ O + Ash	-8.1	-8.7	-12.6	-7.3	-17.2	-20.1	-20.0	-10.5	-9.5	-7.3	-18.2	-16.5	-13.6	-11.2	4.6	2.3	3.4	3.4
Unconv. NAP Coal	10.2	12.1	6.9	10.9	16.7	16.9	20.8	11.7	26.9	7.5	9.1	8.2	11.9	6.9	21.2	25.7	23.5	23.5
Solvent Recycle, %																		
Actual	87.5	87.4	81.3	80.0	92.1	96.7	93.4	102.7	97.4	100.5**	85.4	96.2**	97.7	87.7	90.9	92.6	91.7	91.7
Possible (Calc.)	100.9	104.9	100.0	106.6	100.6	105.2	101.9	105.6	101.2	101.2	102.4	103.1	100.9	101.5	93.4	93.6	93.5	93.5
Material Balance, %	98.0	104.4	100.0	101.1	98.5	98.8	97.6	97.7	99.2	97.2	97.9	97.5	98.4	99.5	96.4	100.8	98.6	98.6
Conditions																		
Temperatures, °F																		
Preheater Outlet	723	730	738	738	747	765	748	763	748	724	725	725	730	684	743	752	748	748
Dissolver Inlet	714	723	729	729	-	703	699	702	728	719	-	-	-	787	719	721	720	720
R-1A 3 ft	760	752	773	762	-	-	-	-	-	-	-	-	-	850	862	-	-	-
R-1A 15 ft	833	828	835	820	-	-	-	-	-	-	-	-	-	850	862	-	-	-
R-1B 3 ft	-	-	-	-	811	775	809	770	738	714	716	715	804	-	768	770	769	769
R-1B 15 ft	828	831	824	811	-	894	853	897	864	757*	848	856	832	796	-	800	802	801
Dissolver Outlet	637	639	635	640	-	843	855	-	-	-	-	-	-	770	850	806	806	806
Flash Preheat	579	580	574	572	538	562	565	554	525	533	532	532	546	565	613	627	613	623
Flash Vapor																		
Pressures																		
Dissolver, psig	2500	2500	2500	2500	2500	2500	2500	2500	2500	2500	2500	2500	2500	2500	1500	1500	1500	1500
Inter, Sep, psig	330	300	325	330	320	304	330	320	330	330	320	325	330	350	250	150	200	200
Vac. Flash, Torr	15	15	15	14	15	15-20	15-20	15-20	15	15-20	15-20	15-20	15	15	15	15	15	15
S-Ls System in Use?	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No	No	No	No	No

* 7 ft. level

** Excess comes from deashing solvent, 7.5%.

Table 10 - Summary of Liquefaction Tests

Yield Period	M-16A	M-17A	M-17B	M-20A	M-21A	M-21B	M-21D	M-21E	M-22A	M-23A	M-23B
Symbols	◇	◇	→	△	■	→	→	→	◇	△	→
Hours on Coal at End of YP	19	29	41	19	24	36	76	88	24	27	47
During Run	914	950	962	1044	1071	1083	1123	1135	1159	1199	1219
Cumulative	1	1	1	1	1	1	1	1	1	1	1
No. of Reactors	48	45	37	48	47	46	48	45	48	49	49
Coal Charged, Lbs/Hr	435	535	537	478	630	605	612	608	558	554	559
Gas Charged, SCF/Hr	1.76	1.81	2.16	1.84	1.94	1.87	1.87	1.98	1.89	1.80	1.76
Solvent/Coal Ratio	1.43	1.34	1.27	1.41	1.34	1.39	1.40	1.38	1.44	1.41	1.40
LHSV, Hr ⁻¹	305	374	376	334	440	424	429	425	390	387	390
GHSV, Hr ⁻¹	33.9	31.3	25.7	33.8	32.7	32.4	33.5	31.6	33.8	34.1	34.1
Coal Rate, Lbs/Hr/CF	9.0	12.0	14.6	9.9	13.5	13.1	12.8	13.5	11.6	11.4	11.5
Gas Rate, SCF/Lb Coal	3.5	2.4	2.6	4.5	3.6	3.0	3.7	3.2	1.2	1.6	1.1
Gas Consumed, SCF/Lb Coal											
Yields, Wt % YAF Coal											
Net Gas	39.2	28.0	35.7	41.8	28.7	35.2	30.8	36.5	25.5	27.5	30.3
Net Oil	55.5	67.3	63.7	14.9	51.1	58.4	57.4	60.7	42.3	34.8	36.4
(light Oil)	(2.3)	(13.1)	(13.3)	(-29.8)	(-12.5)	(-0.9)	(-3.0)	(1.2)	(-14.7)	(-23.1)	(-11.4)
(SRL)	(53.2)	(54.2)	(50.4)	(44.7)	(63.6)	(59.3)	(60.4)	(59.5)	(57.0)	(57.9)	(47.8)
Net H ₂ O and Ash	-10.2	-5.9	-5.6	5.1	5.5	-5.7	-1.4	-7.8	6.8	-0.2	2.6
Unconv. YAF Coal	15.5	10.6	6.2	38.2	14.7	12.1	13.2	10.6	25.4	37.9	30.7
Liquid Recycle, %											
Actual	98.8	103.5*	100.6*	80.1	88.4	72.5	67.2	68.3	93.1	86.7	92.2
Possible (Calc.)	100.9	104.6	103.8	88.7	95.8	99.7	99.0	100.4	94.8	92.0	95.9
Solvent (Ex. Lt Oil) Possible	94.6	104.0	94.6	82.5	89.1	92.0	95.4	94.4	90.5	86.4	93.1
Material Balance, %	96.7	100.1	97.9	98.1	101.5	95.2	101.9	99.6	97.8	99.6	97.0
Conditions											
Temperatures, °F											
Preheater Outlet	744	747	745	787	741	743	746	743	752	764	774
Dissolver Inlet	NIU	752	774	830	NIU	740	746	740	748	741	746
R-1A 15 ft	NIU	802	826	877	NIU	NIU	NIU	NIU	NIU	NIU	NIU
R-1B 15 ft	NIU	802	826	877	NIU	NIU	NIU	NIU	NIU	NIU	NIU
R-1C 15 ft	NIU	802	826	877	NIU	NIU	NIU	NIU	NIU	NIU	NIU
R-1D 15 ft	NIU	802	826	877	NIU	NIU	NIU	NIU	NIU	NIU	NIU
Dissolver Outlet	849	849	849	876	823	832	828	822	765	831	825
Flash Preheat	633	639	660	644	639	639	646	649	625	646	637
Flash Vapor	584	584	550	472	513	513	525	525	504	524	522
Pressures											
Dissolver, psig	2500	2500	2500	2500	2000	2000	2000	2000	1500	1500	1500
Inter. Sep. psig	250	250	250	250	250	250	250	250	250	250	250
Vac. Flash, Torr	15	15	15	15	15	15	15	15	15	15	15
S-L/S System in Use ?	No	Yes	Yes	No	No	No	Yes	Yes	No	No	No
H ₂ /CO Ratio	1/3	3/1	3/1	Pure H ₂	3/1	3/1	3/1	3/1	3/1	3/1	3/1
CO ₂ Yield, Wt % YAF Coal	67.8	35.4	43.8	16.9	41.1	45.0	41.8	47.0	25.2	30.7	32.1
C1-C3 Yield, Wt % YAF Coal	15.7	5.9	10.6	27.3	6.9	7.4	6.7	7.4	7.2	8.6	8.9
*From SLS Solvent, %	-	3.9	6.3	-	-	-	-	-	-	-	-

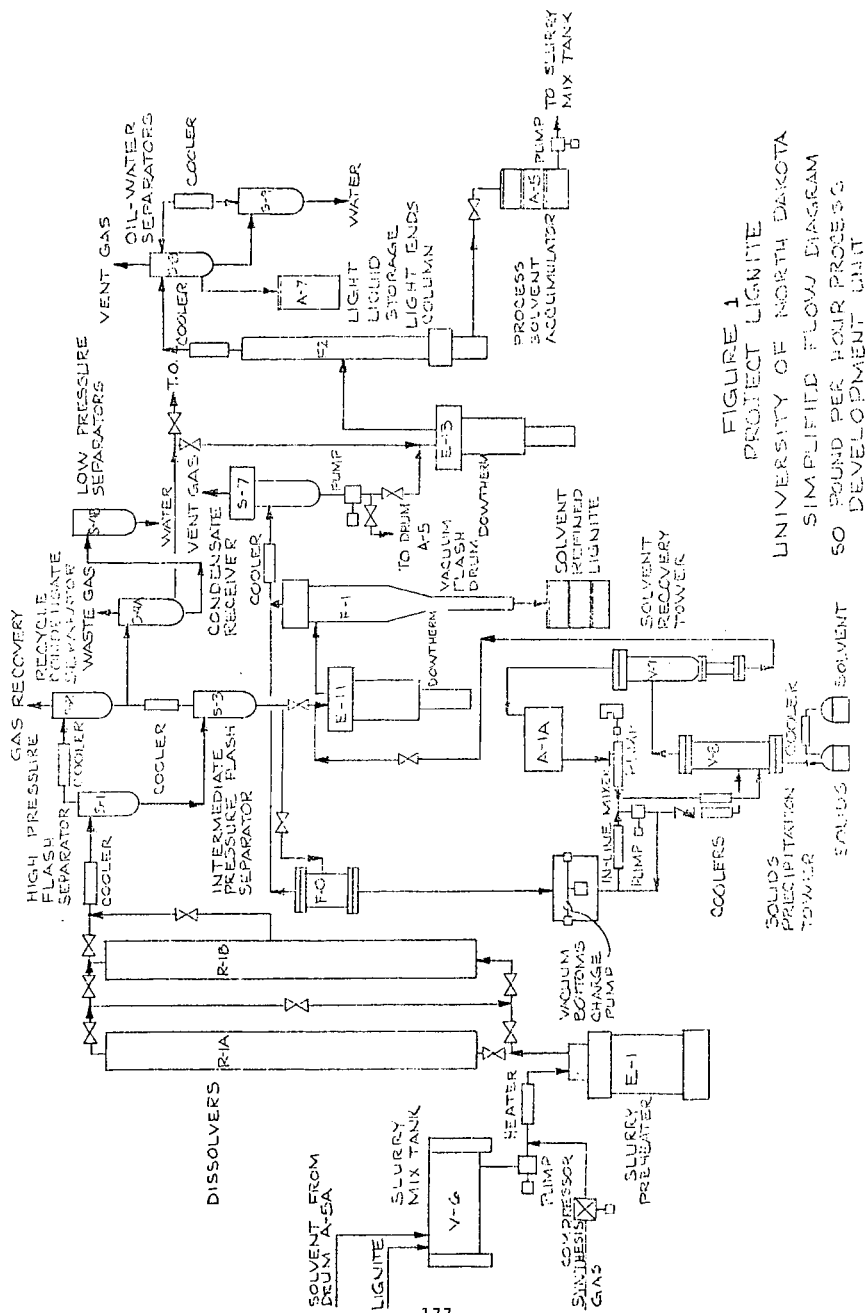


FIGURE 1
PROJECT LIGNITE
UNIVERSITY OF NORTH DAKOTA
SIMPLIFIED FLOW DIAGRAM
50 POUND PER HOUR PROCESS
DEVELOPMENT UNIT

LBS/HR	
LIGNITE 44.8	
GAS 11.5	
LIQUEFACTION SOLVENT (Recycled) 81.3	
TOLUENE DEASHING SOLVENT (Recycled) 111.9	
GROSS INPUT	250

LBS/HR	
PRODUCTS 18.9	
RESIDUE 18.0	
GAS 19.4	
LIQUEFACTION SOLVENT (Recycled) 81.3	
TOLUENE DEASHING SOLVENT (Recycled) 111.9	
GROSS OUTPUT	250

LBS/HR	
LIGNITE 44.8	
M.A.F. LIGNITE 28.1	
ASH 2.6	
MOISTURE 14.1	
GAS 11.5	
CO 9.4	
H ₂ 2.1	
INPUT	
HYDROCARBONS 18	
CO ₂ 9.9	
CO 5.8	
H ₂ 1.9	
OUTPUT	
WATER 12.4	
ASH 2.6	
UNCONVERTED 3.0	
ORGANIC LIQUIDS 3.7	
SRL 15.2	
PRODUCTS 18.9	
RESIDUAL STREAMS 18.0	
GAS 19.4	

FIGURE 2-GROSS MATERIAL BALANCE, RUN 17A

FIGURE 3-NET MATERIAL BALANCE, RUN 17A

FIGURE 4

CONVERSION AND YIELDS VS. MAXIMUM DISSOLVER TEMPERATURE
(1.0 H₂/CO RATIO, 2500 psig, 1.27-1.60 LHSV, 1.59-2.26
SOLVENT/COAL RATIO)

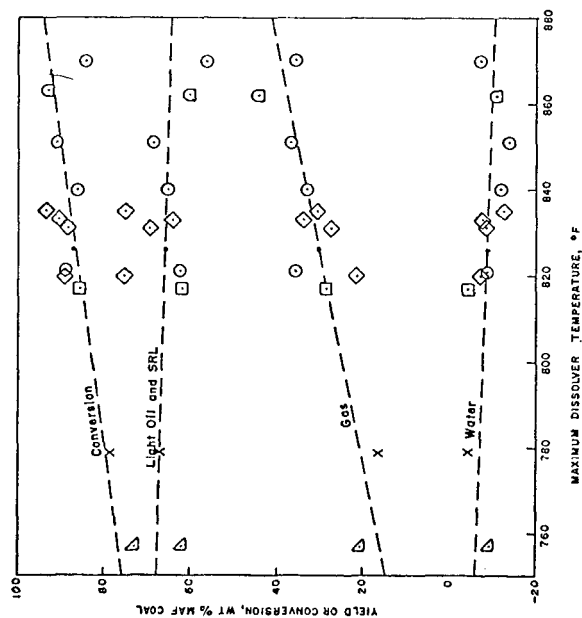


FIGURE 5

CONVERSION AND YIELDS ADJUSTED TO 826° F
MAXIMUM DISSOLVER TEMPERATURE VS. LHSV
(1.0 H₂/CO RATIO, 2500 psig, 826° F, 1.59-2.26
SOLVENT/COAL RATIO)

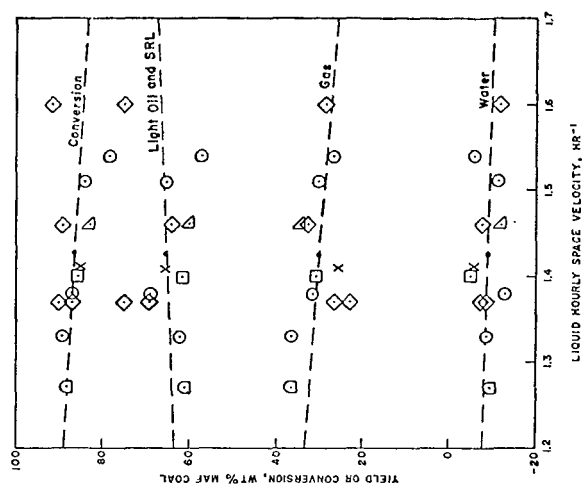


FIGURE 6

CONVERSION AND YIELDS ADJUSTED TO 826° F
MAXIMUM DISSOLVER TEMPERATURE AND 1.425 LHSV
VS. SOLVENT/COAL RATIO

(1.0 H₂/CO RATIO, 2500 psig, 826°F, 1.425 LHSV)

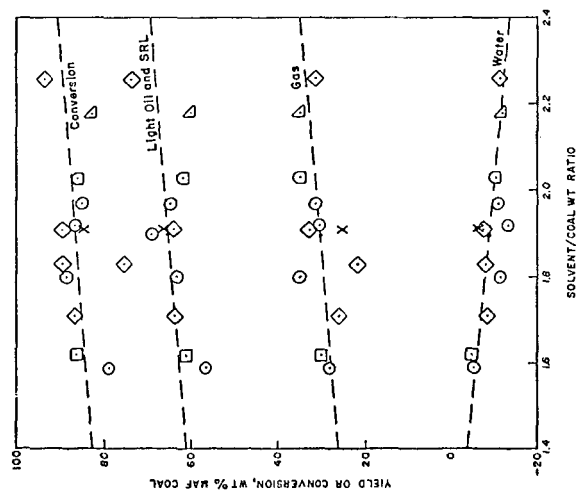


FIGURE 7

SOLVENT RECOVERY vs. MAXIMUM DISSOLVER TEMPERATURE
2500 psig, 1/1 H₂/CO Ratio, ~1.4 LHSV, ~1.9 Solvent/Coal
Ratio

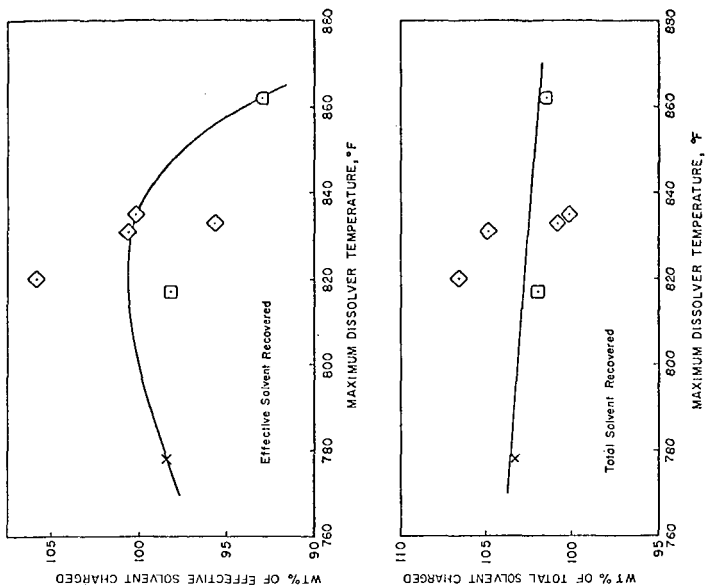


FIGURE 8

CONVERSION AND YIELDS vs. DISSOLVER PRESSURE
(Adjusted to 820° F Maximum Dissolver Temperature,
1.37 LHSV, and 1.91 Solvent to Coal Ratio)

3/1 H₂/CO Ratio

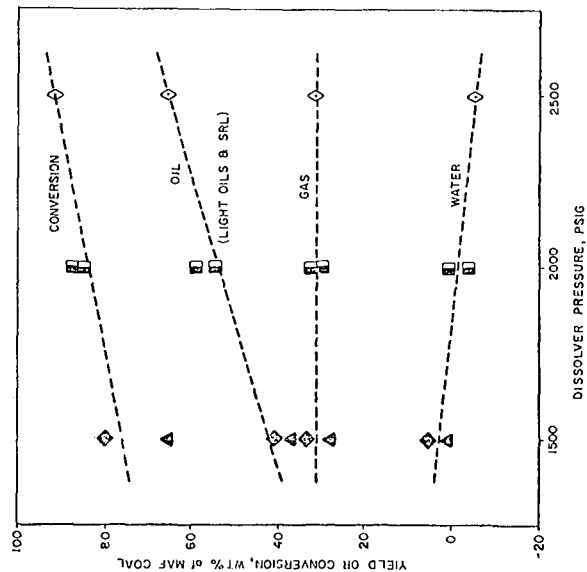


FIGURE 9

SOLVENT RECOVERY vs. DISSOLVER PRESSURE
(Adjusted to 820° F Maximum Dissolver Temperature, 1.37 LHSV,
and 1.91 Solvent/Coal Ratio)

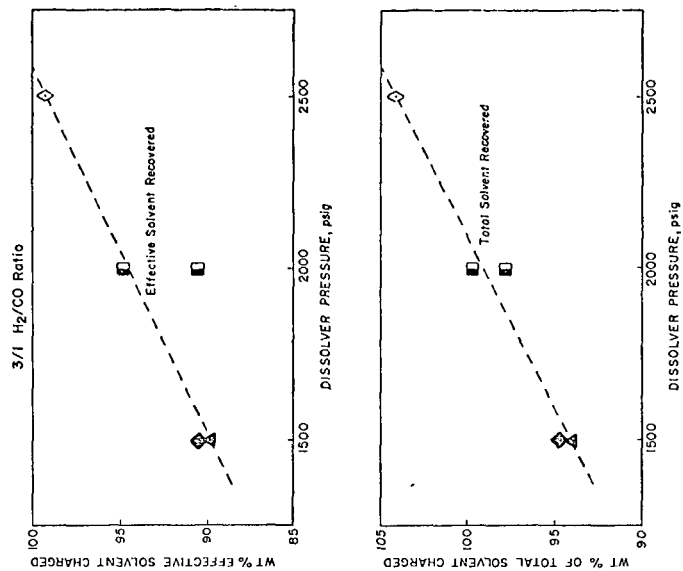


FIGURE 10

CONVERSION AND YIELDS vs MOL % H₂ IN CHARGE GAS
(Adjusted to 835°F Maximum Dissolver Temperature,
1.4:1 LHSV, and 1.91 Solvent/Coal Ratio)
2500 psig Dissolver Pressure

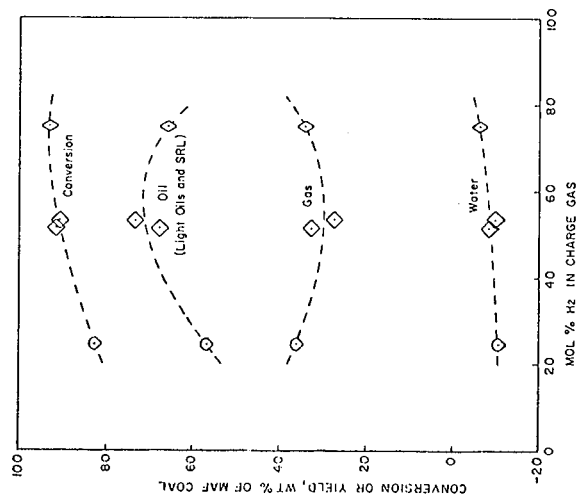
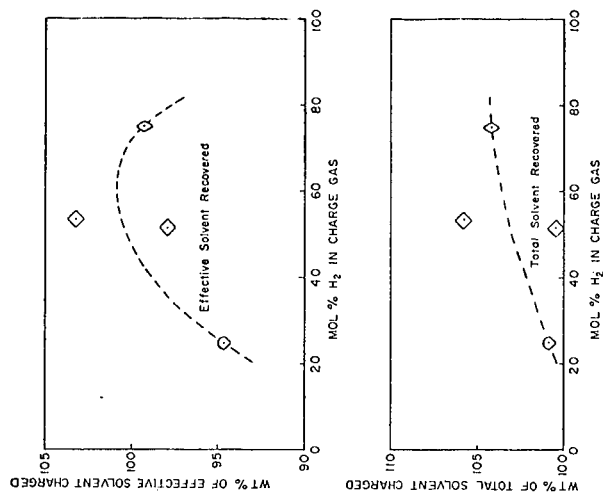


FIGURE 11

SOLVENT RECOVERY vs MOL % H₂ IN CHARGE GAS
(Adjusted to 835°F Maximum Dissolver Temperature,
1.4:1 LHSV, and 1.91 Solvent/Coal Ratio)
2500 psig Dissolver Pressure



MINERAL MATTER EFFECTS IN COAL LIQUEFACTION

1. AUTOCLAVE SCREENING STUDY*

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INTRODUCTION

Several processes have been developed for converting coals to liquid fuels. In order to produce a pumpable, environmentally acceptable fuel, it is necessary to understand how the properties of the feed coals affect the composition of the resulting liquid products -- especially the viscosity and sulfur content. It has been shown, for example, that the petrographic (maceral) composition of the feedstock plays a significant role in coal conversion processes.¹⁻² The role of mineral matter, however, has not been as clearly defined or as extensively studied.

Mukherjee and Chowdhury showed that the extent of conversion to liquid products increased with both ash content and with the concentration of iron and titanium.³ Iron, as contained in the residues from coal liquefaction experiments, has been shown to increase the hydrogen transfer capacity of anthracene oil.⁴ It was found that pyrite, and solids from the SRC (Solvent Refined Coal) process had a significant effect on the hydrogenation of creosote oil, and that coal ash, reduced iron and SRC solids exhibited a considerable activity for desulfurization.⁵ In that same study, it was shown that the conversion of a Kentucky No. 9/14 coal to cresol-solubles was dependent upon mineral content.

It is clear from the published data that coal minerals may play a significant role in liquefaction processes. It is, therefore, important to establish predictive correlations between mineral content and liquid product composition. Our studies on matter effects in coal hydroliquefaction have been directed toward this objective. We utilized batch autoclave experiments, under closely controlled conditions of temperature, heating rate, pressure and residence time, to evaluate the reactivities of several coals having similar petrographic composition but widely varying mineral content. This paper will present the autoclave screening data that have been obtained in the first phase of our program. We will relate viscosity, sulfur content and conversion to the mineral content of the feed coals.

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EXPERIMENTAL

The coals used in the autoclave screening studies are listed in Table 1. They were pulverized to minus 100 mesh and stored under argon in polyethylene containers. Each sample was thoroughly homogenized prior to use. Proximate, ultimate and sulfur forms analyses are given in Table 2, and the petrographic (maceral) composition of each sample is shown in Table 3. All of the coals used in this study were high volatile bituminous, with widely varying sulfur and ash contents. Most of the samples had high (>80%) vitrinite contents and were relatively low in fusinite and micrinite. It was felt that these coals would provide a valuable test matrix for studying mineral matter effects because they were all of similar rank, geological origin and petrographic composition, but varied considerably in ash content.

Mineral matter content was determined by x-ray diffraction analysis of low temperature ash.⁶⁻⁷ The samples were prepared by ashing the coals at a low temperature (<100°C) in a radiofrequency field, using a Tracerlab Low Temperature Asher (LTA 600). The RF power was 200-250 watts, the oxygen flow rate 60-80 cm³/min and the total ashing time 48-96 hours. Calibration curves for the quantitative analysis of quartz, calcite and pyrite were prepared, using nickel oxide as an internal standard. The clays were analyzed by using talc as an internal standard. Kaolinite was distinguished from the mixed layer clays by expanding the basal layers of the latter with ethylene glycol. Results of these analyses are given in Table 4 as a weight percent of the coal on a dry basis. Also included in this table for comparison, are values for pyrite that were computed from the pyritic sulfur content shown in Table 2.

The solvent (vehicle) used for the liquefaction runs in this study was creosote oil (No. 4 cut), which was obtained from the Reilly Tar and Chemical Co. This oil had a specific gravity of 1.12 and a boiling range of 270-400°C.

All of the experiments were carried out in a one-liter (Autoclave Engineers, Inc.) magne-drive autoclave, equipped with a turbine agitator. A stainless steel liner, with an effective working volume of approximately 0.7 liter, was used in order to facilitate loading and unloading, and to improve the material accountability. The inside surface of this liner was cleaned by bead-blasting after each run. The temperature was monitored and controlled by dual chromel-alumel thermocouples; the pressure was monitored with a 0-5000 psig transducer. The temperature and pressure were recorded continuously.

In a typical experiment, the autoclave (with steel liner in place) was charged with 50.0 g (daf basis) of coal and 115.0 g of creosote oil, and the mixture was stirred at 500 rpm. The system was purged with inert gas and leak tested at 2000 psig. The system was then purged with hydrogen, charged to the desired initial (cold) pressure, which was controlled to ± 2 psig, and leak tested again. The autoclave contents were heated to the desired operating temperature (nominally 430°C) over a period of approximately one hour. The temperature during the (30 min.) run was manually controlled to $\pm 3^\circ\text{C}$. No additional hydrogen was added during the run, and the pressure dropped gradually as the hydrogen was consumed. At the end

Table 1
 Coals Used in the Autoclave Screening Study

Sample No.	State	Seam	Mine
G98-76	Kentucky	No. 11	Fies
G98-64	Kentucky	No. 11	Homestead
G98-54	West Virginia	Pittsburgh	Ireland
G98-57	Illinois	No. 6	Orient 4
G98-82	Pennsylvania	Pittsburgh	Bruceton
G98-71	Kentucky	Elkhorn No. 3	Guaranty

Table 2

Analyses of Coals Used in the Autoclave Screening Study^a

	Kentucky No. 11 (Fies)	Kentucky No. 11 (Homestead)	West Virginia	Illinois No. 6	Pennsyl- vania	Kentucky Elkhorn No. 3
<u>Proximate Analysis</u>						
Volatile Matter	39.01	39.24	41.32	36.69	38.11	36.83
Fixed Carbon	43.80	47.87	48.73	52.60	58.19	58.81
Ash	17.19	12.89	9.95	10.71	3.70	4.36
<u>Ultimate Analysis</u>						
Carbon	64.77	68.80	72.64	71.48	81.71	80.36
Hydrogen	4.65	4.78	5.19	4.89	5.35	5.45
Nitrogen	1.24	1.43	1.27	1.45	1.64	1.88
Sulfur	6.11	4.88	4.44	3.00	1.05	0.78
Oxygen (difference)	5.95	7.22	6.45	8.47	6.49	7.17
Ash	17.19	12.89	9.95	10.71	3.70	4.36
<u>Sulfur Forms</u>						
Pyritic	3.68	2.41	1.48	1.27	0.30	0.08
Sulfate	0.11	0.11	0.41	0.09	0.02	0.00
Organic	2.32	2.36	2.55	1.64	0.73	0.70
Total	6.11	4.88	4.44	3.00	1.05	0.78

^a All data are on a dry basis.

Table 3

Petrographic Composition of Coals Used in the Autoclave Screening Study^a

Sample	Macerals ^a (volume %)						
	V	PV	F	SF	MM	GM	R
Kentucky No. 11 (Fies)	86.9	4.1	2.1	3.1	0.6	1.4	1.8 0.0
Kentucky No. 11 (Homestead)	87.7	3.6	3.1	3.0	0.4	1.2	1.0 0.0
West Virginia	85.7	3.6	2.9	3.3	0.8	2.3	1.4 0.0
Illinois No. 6	89.8	4.3	1.9	0.9	0.2	1.6	1.2 0.1
Pennsylvania	81.9	4.9	2.8	4.3	1.6	1.8	2.7 0.0
Kentucky Elkhorn No. 3	74.7	9.3	1.4	2.5	0.9	5.4	5.3 0.5

^aIn these columns, V = vitrinite, PV = pseudovitrinite, F = fusinite, SF = semifusinite,

MM = massive micrinite, GM = granular micrinite, E = exinite, R = resinite.

Table 4

Mineral Composition of Low Temperature Ash

Sample	% Dry Basis						Pyrite calculated from pyritic sulfur (% dry basis)
	mm ^a	Pyrite	Quartz	Calcite	Kaolinite	Mixed Layer Clays	
Kentucky No. 11 (Fies)	20.90	5.43	3.34	n.d. ^b	0.21	11.92	6.88
Kentucky No. 11 (Homestead)	15.70	4.55	2.50	1.10	0.32	7.23	4.51
West Virginia	13.82	3.26	1.46	n.d.	1.19	7.91	2.77
Illinois No. 6	12.95	2.80	2.20	0.78	0.82	6.35	2.37
Pennsylvania	5.18	0.53	0.54	n.d.	0.33	3.78	0.56
Kentucky Elkhorn No. 3	5.62	n.d.	trace	n.d.	2.00	3.50	0.15

^a mm = mineral matter^b n.d. = not detected by x-ray diffraction techniques

of the experiment the furnace was lowered. Stirring was continued, and the contents of the autoclave were allowed to cool to room temperature overnight. The overhead gases were slowly vented through two caustic scrubbers, and the system was purged with inert gas. The reaction products were removed and weighed. A summary of the operating conditions used in all of the autoclave screening experiments is given in Table 5.

The liquid product from each run was filtered hot (60-100°C) under nitrogen (80-120 psig), using a jacketed (brass) pressure filter. In some cases, due to the high viscosity of the liquid or the gelatinous consistency of the residue, it was not possible to filter the product. In these situations, centrifugation (40 min at 2500 rpm) was used to accomplish solids separation, but this was not as effective for ash removal as was filtration.

The filter cake (residue), consisting of unreacted coal and mineral matter, was washed several times with acetone. It was then dried overnight in a vacuum oven at 105°C. The resulting dry residue, a freely flowing powder, was ashed at 775°C. The extent of conversion to liquid products, on a dry, ash-free (daf) basis, was then calculated by means of a forced ash balance.⁸

The viscosity of the filtered liquid product was measured at 60°C with a Brookfield viscometer that was equipped with a small sample adapter. The estimated precision, based on replicate measurements on certified standards, was $\pm 5\%$.

The sulfur content of the filtered liquid product was obtained with a Leco automatic sulfur analyzer, using a combustion iodometric procedure. Replicate analyses were carried out on samples whose sulfur contents had been independently determined by the standard Eschka method (ASTM D271-70). The Leco results were within $\pm 0.05\%$ (absolute) of the Eschka data.

RESULTS AND DISCUSSION

The data from the autoclave screening experiments are shown in Table 6. All of the liquid products were filterable except for the one obtained from the Kentucky Elkhorn coal, in which case centrifugation was required for solids separation. The viscosities of the liquid products varied by more than an order of magnitude. The observed increases in viscosity appeared to correlate well with the marked decreases in the mineral content of the feed coals (Table 6). Since the coals had similar maceral compositions (Table 3) and all autoclave runs were carried out under closely controlled conditions, it may be concluded that the variations in product viscosity were the result of a mineral matter effect. Thus, changes in mineral composition had a substantial effect on the quality (e.g., pumpability) of the resulting liquid product.*

*Ancillary experiments have shown that the product viscosity was strongly dependent upon the preasphaltene (pyridine soluble-benzene insoluble) content,⁹ which, in turn, was related to the mineral content of the feed coals.

Table 5

Conditions Used in the Autoclave Screening Experiments

Coal charge	:	50.0 g (daf basis)
Solvent (creosote oil) charge	:	115.0 g
Coal particle size	:	through 100 mesh
Initial (cold) pressure	:	1000 psig H ₂
Heatup time	:	≈ 60 min
Temperature (nominal)	:	430°C
Reaction time (nominal)	:	30 min
Mixing speed	:	500 rpm

Table 6

Results of Autoclave Screening Study^a

Run No. G98-	76	64	54	57	82	71
Coal	Kentucky No. 11 (Fies)	Kentucky No. 11 (Homestead)	West Virginia	Illinois No. 6	Pennsyl- vania	Kentucky Elkhorn No. 3
Mineral matter ^b (%)	20.90	15.70	13.82	12.95	5.18	5.62
Pyrite ^b (%)	5.43	4.55	3.26	2.80	0.53	0.15
Organic sulfur ^b (%)	2.32	2.36	2.55	1.64	0.73	0.70
Temperature (°C)	432	430	429	429	429	433
Initial pressure (psig, 25°C)	999	1000	1000	1001	1000	999
Operating pressure ^c (psig)	1701	1758	1730	1779	1761	1839
Conversion ^d (%)	93	94	88	87	84	62
Filtered liquid product						
Sulfur (%)	0.65	0.68	0.69	0.55	0.43	0.44 ^e
Viscosity (cps @ 60°C)	75	108	124	278	456	761 ^e
Organic Sulfur Removed ^f (%)	72	71	73	66	41	37

^aAll runs in creosote oil solvent; solvent : coal = 2.3.^bFeed coal, dry basis; mineral matter and pyrite from low temperature ash data, except for Kentucky Elkhorn where pyrite was calculated from pyritic sulfur content.^cMaximum pressure at operating temperature.^dDry, ash-free (daf) basis.^eCentrifuged liquid product.^f $\left[\frac{S_{\text{coal}} (\text{organic}) - S_{\text{product}}}{S_{\text{coal}} (\text{organic})} \right]$

It may be assumed that the sulfur in the liquid product was primarily organic sulfur, since the inorganic forms (pyritic and sulfate) were concentrated in the insoluble residues. From the data shown in Table 6, it can be seen that the liquids with the lowest sulfur contents were obtained from the coals that had the lowest organic sulfur contents. The fractional decrease in organic sulfur, however, was highest for the Kentucky No. 11, West Virginia and Illinois No. 6 coals. Thus, the coals with the highest mineral contents appeared to be the most reactive ones with respect to organic sulfur removal. This observation is in agreement with the work reported by Tarrer, *et al.*, where it was shown that certain coal minerals catalyzed the hydrodesulfurization of creosote oil.⁵ Our data (Table 6) would suggest that pyrite could have been active in this respect, but other work has shown that pyrite may not be active for desulfurization.^{5,10} Further experimental work will be required to establish these ideas in a more quantitative manner.

The percent conversion to liquid products were, with the exception of the Kentucky Elkhorn coal, fairly high (Table 6). Since coal dissolution is very rapid under the conditions of temperature, pressure and residence time used in this study,⁸ and since high-vitrinite coals are reactive in liquefaction processes,² it is not surprising that the conversions were high. The somewhat greater conversion for the Kentucky No. 11 coals could have been a result of the increased mineral content, but it is not clear that the observed differences were statistically significant. The extremely low reactivity of the Elkhorn coal, however, was probably due to the considerably lower vitrinite content.

The autoclave screening study has provided data that show a good correlation between mineral composition of the feed coal and product quality (sulfur content and viscosity). In order to pursue these concepts in greater detail, several experiments have been initiated with coals (Illinois No. 6 and Kentucky No. 11) in which the mineral content has been purposefully altered. This was accomplished by: (1) adding pure mineral constituents to the feed coal; and (2) removing mineral matter by both chemical (acid extraction) and physical (froth flotation) techniques. Preliminary data have confirmed several of the tentative conclusions reached in the autoclave screening study. These results will be documented when complete.

SUMMARY

Several high-volatile bituminous coals were hydrolified, in a one-liter autoclave, at a temperature of 430°C, initial (cold) H₂ pressure of 1000 psig and residence time of 30 min. All experiments were carried out in creosote oil as the solvent, at a solvent:coal ratio of 2.3:1. The feed coals ranged in mineral content from 21% to 5%, and in sulfur content from over 6% to under 1%. The coals had similar maceral distributions, and most were vitrinite-rich (>85%). Conversions, calculated by an ash balance on the acetone-washed residues, varied from 62 to 94%. The liquid products were assessed in terms of sulfur content and (Brookfield) viscosity. The sulfur contents ranged from 0.43 to 0.69%; the viscosities (at 60°C) varied from 75 to 761 cps. A good correlation was found between the mineral content of the feed coal and the extent of organic sulfur removal and product viscosity. The highest conversions were found for the coals having the highest mineral contents.

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